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Essential Graduate Physics
Lecture Notes and Problems

Beta version

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Part QM: Quantum Mechanics

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Chapter 1. Introduction

This introductory chapter briefly reviews the major motivations for quantum mechanics. Then its simplest formalism - Schrödinger's wave mechanics - is described, and its main features are discussed. Much of this material (perhaps except for the last section) may be found in undergraduate textbooks.¹

1.1. Experimental motivations

By the beginning of the 1900s, physics (which by that time included what we now know as nonrelativistic classical mechanics, classical statistics and thermodynamics, and classical electrodynamics including geometric and wave optics) looked as an almost completed discipline, with a lot of experimental observations explained, and just a couple of mysterious “dark clouds”² on the horizon. However, the rapid technological progress and the resulting fast development of experimental techniques have led to a fast multiplication of observed phenomena that could not be explained on the classical basis. Let me list the most consequential of those experimental findings.

(i) Blackbody radiation measurements, started by G. Kirchhoff in 1859, have shown that in the thermal equilibrium, the power of electromagnetic radiation by a fully absorbing (“black”) surface per unit frequency interval drops exponentially at high frequencies. This is not what could be expected from the combination of the classical electrodynamics and statistics, which predicted an infinite growth of the radiation density with frequency. Indeed, classical electrodynamics shows³ that electromagnetic field modes in free space evolve in time as harmonic oscillators, and that the density of these modes in a large volume $V \gg \lambda^3$ per small frequency interval is

$$dN = 2V \frac{dV_k}{(2\pi)^3} = 2V \frac{4\pi k^2 dk}{(2\pi)^3} = V \frac{\omega^2}{\pi^2 c^3} d\omega, \quad (1.1)$$

where $c \approx 3 \times 10^8$ m/s is the free-space speed of light, ω its frequency, $k = \omega/c$ the free-space wave number, and $\lambda = 2\pi/k$ is the radiation wavelength. On the other hand, classical statistics⁴ predicts that in the thermal equilibrium at temperature T , the average energy E of each 1D harmonic oscillator should equal $k_B T$, where k_B is the Boltzmann constant.⁵

¹ For remedial reading, I can recommend the following textbooks (in the alphabetical order): S. Gasiorowicz, *Quantum Physics*, 3rd ed., Wiley, 2003; D. Griffith, *Quantum Mechanics*, 2nd ed., Pearson Prentice Hall, 2005; and R. Liboff, *Introductory Quantum Mechanics*, 3rd ed., Addison-Wesley, 1998.

² This expression was used in a 1900 talk by Lord Kelvin (born W. Thomson) in reference to the blackbody radiation measurements and Michelson-Morley experiment results, i.e. the precursors of the quantum mechanics and relativity theory.

³ See, e.g., EM Sec. 7.9. The degeneracy factor 2 in Eq. (1) is due to two possible polarizations of transverse electromagnetic waves. For waves of other physical nature, which obey with the linear (“acoustic”) dispersion law, similar relations are also valid, though possibly with a different degeneracy factor - see, e.g., CM Sec. 7.7.

⁴ See, e.g., SM Sec. 2.2.

⁵ In the SI units, used through these notes, $k_B \approx 1.38 \times 10^{-23}$ J/K. Note that in many theoretical papers (and in the SM part of my notes), k_B is taken for 1, i.e. temperature is measured in energy units.

Combining these two results, we readily get the so-called *Rayleigh-Jeans formula* for the average electromagnetic wave energy per unit volume:

$$u \equiv \frac{1}{V} \frac{dE}{d\omega} = \frac{k_B T}{V} \frac{dN}{d\omega} = \frac{\omega^2}{\pi^2 c^3} k_B T, \quad (1.2)$$

that diverges at $\omega \rightarrow \infty$. On the other hand, the blackbody radiation measurements, improved by O. Lummer and E. Pringsheim, and also H. Rubens and F. Kurlbaum to reach a 1%-scale accuracy, were compatible with the phenomenological law suggested in 1900 by Max Planck:

$$u = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1}. \quad (1.3a) \quad \text{Planck radiation law}$$

The law may be reconciled with the fundamental Eq. (1) if the following replacement is made for the average energy of each field oscillator:

$$k_B T \rightarrow \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1}, \quad (1.3b)$$

with a constant factor

$$\hbar \approx 1.055 \times 10^{-34} \text{ J} \cdot \text{s}, \quad (1.4) \quad \text{Planck's constant}$$

now called *Planck's constant*.⁶ At low frequencies ($\hbar \omega \ll k_B T$), the denominator in Eq. (3) may be approximated as $\hbar \omega / k_B T$, so that the average energy (3b) tends to its classical value $k_B T$, and the Planck law (3a) reduces to the Rayleigh-Jeans formula (2). However, at higher frequencies ($\hbar \omega \gg k_B T$), Eq. (3) describes the experimentally observed rapid decrease of the radiation density – see Fig. 1.

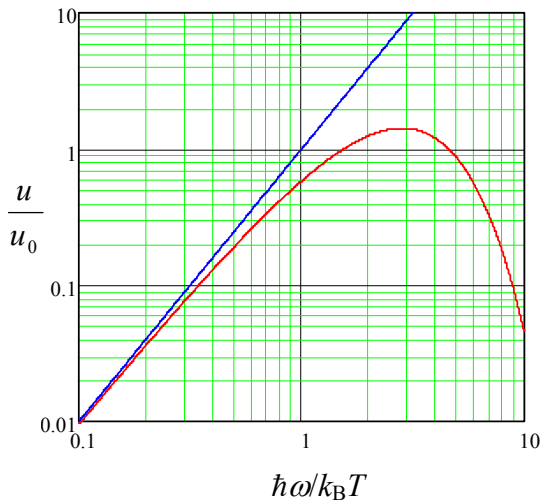


Fig. 1.1. Blackbody radiation density u , expressed in units of $u_0 \equiv (k_B T)^3 / \pi^2 \hbar^2 c^3$, as a function of frequency, according to: the Rayleigh-Jeans formula (blue line) and the Planck law (red line).

(ii) The photoelectric effect, experimentally discovered in 1887 by H. Hertz, shows a sharp lower bound on the frequency of light that may kick electrons out from metallic surfaces, regardless of

⁶ M. Planck himself wrote $\hbar \omega$ as $h \nu$, where $\nu = \omega / 2\pi$ is the “cyclic” frequency, measured in Hz (periods per second), so that in early texts the term “Planck’s constant” referred to $h \equiv 2\pi \hbar$, while $\hbar$ was called “the Dirac constant” for a while.

the light intensity. Albert Einstein, in the first of his three famous 1905 papers, noticed that this threshold $\omega_{\min}$ could be readily explained assuming that light consisted of certain particles (now called *photons*) with energy

$$E = \hbar\omega = h\nu, \quad (1.5)$$

Energy
vs
frequency

with the same Planck's constant that participates in Eq. (3).⁷ Indeed, with this assumption, at the photon absorption by the surface, its energy $E = \hbar\omega$ is divided between a fixed energy W (now called the *workfunction*) of electron binding inside the metal, and the residual kinetic energy $mv^2/2 > 0$ of the freed electron – see Fig. 2. In this picture, the frequency threshold finds a natural explanation as $\omega_{\min} = W/\hbar$.⁸ Moreover, as was shown by S. Bose in 1924, Eq. (5) readily explains⁹ Planck's law (3).

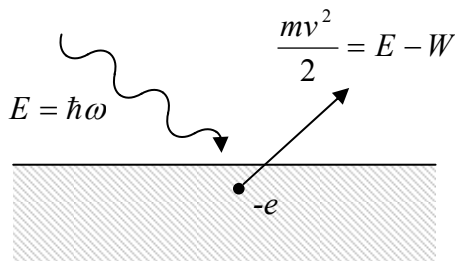


Fig. 1.2. Einstein's explanation of the photoelectric effect's frequency threshold.

(iii) The discrete frequency spectra of radiation by excited atomic gases, known since the 1600s, could not be explained by classical physics. (Applied to the planetary model of atoms, proposed by E. Rutherford, it predicts the collapse of electrons on nuclei in $\sim 10^{-10}$ s due to electric dipole radiation of electromagnetic waves.¹⁰) Especially challenging was the observation by J. Balmer (in 1885) that the radiation frequencies of simple atoms may be described by simple formulas. For example, for the simplest atom, hydrogen, all radiation frequencies may be numbered with just two positive integers n and n' :

$$\omega_{n,n'} = \omega_0 \left(\frac{1}{n^2} - \frac{1}{n'^2} \right), \quad (1.6)$$

with $\omega_0 \equiv \omega_{1,\infty} \approx 2.07 \times 10^{16} \text{ s}^{-1}$. The Balmer series, including the value of ω_0 , have found its first explanation in the famous 1913 theory by Niels Bohr, which was a semi-phenomenological precursor for quantum mechanics. In this theory, $\omega_{n,n'}$ is interpreted as the frequency of a photon that obeys the Einstein's formula (5), with its energy $E_{n,n'}$ being the difference between two *quantized* (discrete) energy levels of the atom (Fig. 3):

$$E_{n,n'} = E_{n'} - E_n > 0. \quad (1.7)$$

⁷ As a reminder, A. Einstein received his only Nobel Prize (in 1922) for exactly this work, which essentially started quantum mechanics, rather than for his relativity theory.

⁸ For most metals, W is between 4 and 5 electron-volts (eV), so that the threshold corresponds to $\lambda_{\max} = 2\pi c/\omega_{\min} = ch/W \approx 300 \text{ nm}$ – approximately at the border between the visible light and ultraviolet radiation.

⁹ See, e.g., SM Sec. 2.5.

¹⁰ See, e.g., EM Sec. 8.2.

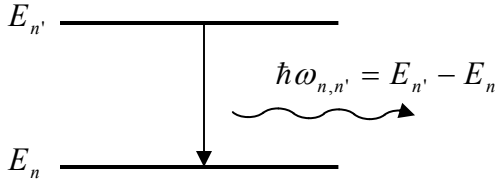


Fig. 1.3. Electromagnetic wave radiation at system's transition between its two quantized energy levels.

Bohr showed that the correct¹¹ expression for the levels (relative to the free electron energy),

$$E_n = -\frac{E_H}{2n^2} < 0, \quad (1.8)$$

Hydrogen
atom's
energy
levels

and the correct value of the so-called *Hartree energy*¹²

$$E_H \equiv 2\hbar\omega_0 = \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \approx 27.2 \text{ eV}, \quad (1.9)$$

Hartree
energy
constant

(where $e \approx 1.602 \times 10^{-19}$ C is the fundamental electric charge, and $m_e \approx 0.911 \times 10^{-30}$ kg is electron's rest mass) could be obtained, with a virtually one-line calculation, from the classical mechanics plus just one additional postulate, equivalent to the assumption that the angular momentum $L = m_e v r$ of the electron moving on a circular trajectory of radius r about hydrogen's nuclei (i.e. proton, assumed to stay at rest), is *quantized* as

$$L = \hbar n, \quad (1.10)$$

Angular
momentum
quantization

where $\hbar$ is again the same Plank's constant (4), and n is an integer. Indeed, in order to derive Eq. (8), it is sufficient to solve Eq. (10) together with the 2nd Newton's law for the rotating electron,

$$m_e \frac{v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}, \quad (1.11)$$

for the electron velocity v and radius r , and then plug the results into the nonrelativistic expression for the full electron's energy

$$E = \frac{m_e v^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}. \quad (1.12)$$

(This nonrelativistic approach to the problem is justified *a posteriori* by the fact the relevant energy scale E_H is much smaller than electron's rest energy, $m_e c^2 \sim 0.5$ MeV.) By the way, the value of r , corresponding to $n = 1$, i.e. to the smallest possible electron orbit,

$$r_B \equiv \frac{\hbar^2}{m_e (e^2 / 4\pi\epsilon_0)} \approx 0.053 \text{ nm}, \quad (1.13)$$

Bohr
radius

¹¹ Besides very small corrections due to the finite ratio of the electron mass m_e to that of the nuclei, and minor spin-orbital and relativistic effects - see Secs. 6.3 and 9.7 below.

¹² Unfortunately, another mane, "Rydberg constant" is also frequently used for either this atomic energy unit or its half, $E_H/2 \approx 13.6$ eV. To add to the confusion, the same term "Rydberg constant" is sometimes used for the reciprocal free-space wavelength ($1/\lambda_0 = \omega_0/2\pi c$) corresponding to frequency $\omega_0 = E_H/2\hbar$.

and called the *Bohr radius*, defines the most important spatial scale of phenomena in atomic, molecular and condensed matter physics - as well as in chemistry and biochemistry.

Now note that the quantization postulate (10) may be presented as the condition that an integer number (n) of certain waves¹³ fits the circular orbit's perimeter $2\pi r = n\lambda$. Dividing both parts of this relation by λ , we see that for this statement to be true, the wave number $k \equiv 2\pi/\lambda$ of the (then hypothetical) de Broglie waves should be proportional to electron's momentum $p = mv$:

Momentum
vs wave
number

$$p = \hbar k . \quad (1.14)$$

(iv) The Compton effect¹⁴ is the reduction of frequency of X-rays at their scattering on free (or nearly-free) electrons – see Fig. 4.

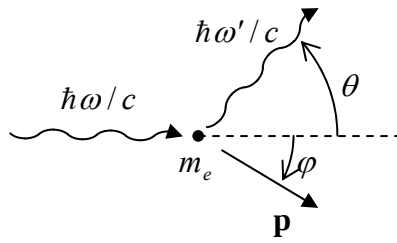


Fig. 1.4. Compton effect.

The effect may be explained assuming that the X-ray photon also has a momentum that obeys the vector-generalized version of Eq. (14):

$$\mathbf{p}_{\text{photon}} = \hbar \mathbf{k} = \frac{\hbar \omega}{c} \mathbf{n}, \quad (1.15)$$

where $\mathbf{k}$ is the *wavevector* (whose magnitude is equal to the wave number k , and direction coincides with that, $\mathbf{n}$, of the wave propagation), and that momenta $\mathbf{p}$ of both the photon and the electron are related to their energies E by the classical relativistic formula¹⁵

$$E^2 = (cp)^2 + (mc^2)^2. \quad (1.16)$$

(For a photon, the rest energy is zero, and this relation is reduced to Eq. (5): $E = cp = \hbar \omega$.) Indeed, a straightforward solution of the following system of three equations,

$$\hbar \omega + m_e c^2 = \hbar \omega' + [(cp)^2 + (m_e c^2)^2]^{1/2}, \quad (1.17)$$

$$\frac{\hbar \omega}{c} = \frac{\hbar \omega'}{c} \cos \theta + p \cos \varphi, \quad (1.18)$$

$$0 = \frac{\hbar \omega'}{c} \sin \theta - p \sin \varphi, \quad (1.19)$$

¹³ This fact was noticed and discussed in detail in 1923 by L. de Broglie, so that instead of discussing wavefunctions, especially of free particles, we are still frequently speaking of *de Broglie waves*.

¹⁴ This effect was observed (in 1922) and explained a year later by A. Compton.

¹⁵ See, e.g., EM Sec. 9.3.

(which describe, respectively, the conservation of the full energy of the photon-electron system, and of two relevant Cartesian components of its full momentum, at the scattering event – see Fig. 4), yields the following result,

$$\frac{1}{\hbar\omega'} = \frac{1}{\hbar\omega} + \frac{1}{m_e c^2} (1 - \cos \theta), \quad (1.20a)$$

which is traditionally represented as the relation between the initial and final values of photon's wavelength $\lambda = 2\pi/k = 2\pi/(\omega/c)$:

$$\lambda' = \lambda + \frac{2\pi\hbar}{m_e c} (1 - \cos \theta) = \lambda + \lambda_c (1 - \cos \theta), \quad \text{with } \lambda_c \equiv \frac{2\pi\hbar}{m_e c}, \quad (1.20b) \quad \text{Compton effect}$$

and is in agreement with experiment.¹⁶

(v) De Broglie wave diffraction. In 1927, following the suggestion by W. Ellassger (who was excited by de Broglie's conjecture of “matter waves”), C. Davisson and L. Germer, and independently G. Thomson succeeded to observe diffraction of electrons on crystals (Fig. 5). Specifically, they have found that the intensity of the elastic reflection from a crystal increases sharply when angle θ between the incident beam of electrons and crystal's atomic planes, separated by distance d , satisfies the following relation:

$$2d \sin \theta = n\lambda, \quad (1.21) \quad \text{Bragg condition}$$

where $\lambda = 2\pi/k = 2\pi\hbar/p$ is the de Broglie wavelength of electrons, and n is an integer. As Fig. 5 shows, this is just the well-known condition¹⁷ that the optical path difference $\Delta l = 2d \sin \theta$ between the de Broglie waves reflected from two adjacent crystal planes coincides with an integer number of λ , i.e. of the constructive interference of the waves.¹⁸

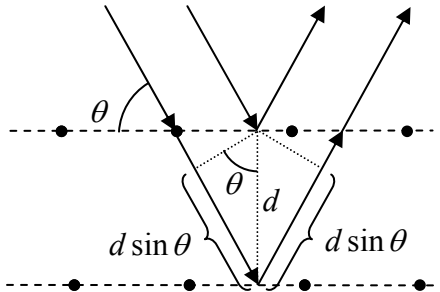


Fig. 1.5. Electron scattering from a crystal lattice.

¹⁶ The constant λ_c , which participates in this relation, is close to 2.46×10^{-12} m and is called the *Compton wavelength* of the electron. This term is somewhat misleading: as the reader can see from Eqs. (17)-(19), no wave in the Compton problem has such a wavelength – either before or after the scattering.

¹⁷ Frequently called the *Bragg condition*, due to the pioneering experiments by W. Bragg with X-ray scattering from crystals (that started in 1912).

¹⁸ Later, spectacular experiments with diffraction and interference of heavier particles, e.g., neutrons and even C_{60} molecules, have also been performed – see, e.g., a review by A. Zeilinger *et al.*, *Rev. Mod. Phys.* **60**, 1067 (1988) and a later publication by O. Nairz *et al.*, *Am. J. Phys.* **71**, 319 (2003). Nowadays, such interference of heavy particles is used for ultrasensitive measurements of gravity – see, e.g., a popular review by M. Arndt, *Phys. Today* **67**, 30 (May 2014), and recent advanced experiments by P. Hamilton *et al.*, *Phys. Rev. Lett.* **114**, 100405 (2015). Moreover, quantum interference between different parts and different quantum states of such macroscopic objects as superconducting condensates of millions Cooper pairs has been observed – see Sec. 3.1 below for details.

To summarize, all the listed effects may be explained starting from two very simple (and similarly looking) formulas: Eq. (5) for photons, and Eq. (15) for both photons and electrons - both relations involving the same Planck's constant. This might give an impression of sufficient experimental evidence to declare light consisting of discrete particles (photons), and, on the contrary, electrons being some “matter waves” rather than particles. However, by that time (the mid 1920s) physics has accumulated overwhelming evidence of *wave* properties of light, such as interference and diffraction. In addition, there was also a strong evidence for lumped-particle (“corpuscular”) behavior of electrons. It is sufficient to mention the famous oil-drop experiments by R. Millikan and H. Fletcher (1909-1913) in that only single (and whole!) electrons could be added to an oil drop, changing its total electric charge by multiples of electron's charge ($-e$) – and never its fraction. It was apparently impossible to reconcile these observations with a purely wave picture, in which an electron and hence its charge need to be spread over the wave, so that its arbitrary part of it could be cut out using appropriate experimental setups.

Thus the founding fathers of quantum mechanics faced a formidable task of reconciling the wave and corpuscular properties of electrons and photons - and other particles. The decisive breakthrough in that task has been achieved in 1926 by Ervin Schrödinger and Max Born who formulated what is now known as either the *Schrödinger picture of nonrelativistic quantum mechanics in the coordinate representation*, or simply as *wave mechanics*. I will now formulate that picture, somewhat disregarding the actual history of its development.

1.2. Wave mechanics postulates

Let us consider a spinless,¹⁹ nonrelativistic point-like particle whose classical dynamics may be described by a certain Hamiltonian function $H(\mathbf{r}, \mathbf{p}, t)$,²⁰ where $\mathbf{r}$ is particle's radius-vector and $\mathbf{p}$ is coordinate.²¹ Wave mechanics of such *Hamiltonian particles* may be based on the following set of postulates²² that are comfortably elegant - though their final justification is given only by the agreement of all their corollaries with experiment.

(i) Wavefunction and probability. Such variables as $\mathbf{r}$ or $\mathbf{p}$ cannot be always measured exactly, even at “perfect conditions” when all external uncertainties, including measurement instrument imperfection, macroscopic fluctuations of the initial state preparation, and unintended particle interactions with its environment, have been removed.²³ Moreover, $\mathbf{r}$ and $\mathbf{p}$ of the same particle can

¹⁹ Actually, in wave mechanics, the spin of the described particle has not to be equal zero. Rather, it is assumed that the *spin effects* are negligible - as they are, for example, for a nonrelativistic electron moving in a region without an appreciable magnetic field.

²⁰ As a reminder, for many systems (including those whose kinetic energy is a quadratic-homogeneous function of generalized velocities, like $mv^2/2$), H coincides with the total energy E – see, e.g., CM Sec. 2.3.

²¹ Note that this restriction is very important. In particular, it excludes from our current discussion the particles whose interaction with environment is *irreversible*, for example it is the viscosity leading to particle's energy decay. Such systems need a more general quantum-mechanical description that will be discussed in Chapter 7.

²² Generally, quantum mechanics, as any theory, may be built on different sets of postulates (“axioms”) leading to the same conclusions. In this text, I will not try to beat down the number of postulates to the absolute minimum, not only because this would require longer argumentation, but chiefly because such attempts typically result in making certain implicit assumptions hidden from the reader – the practice as common as regrettable.

²³ I will imply such perfect conditions until the discussion of particle's interaction with environment, and realistic (“physical”) measurements in Chapter 7.

never be measured exactly simultaneously. Instead, even the *most detailed* description of the particle's state, allowed by Nature,²⁴ is given by a certain complex function $\Psi(\mathbf{r}, t)$, called the *wavefunction*, that generally enables only *probabilistic* predictions of measured values of $\mathbf{r}$, $\mathbf{p}$, and other directly measurable variables (in quantum mechanics, called *observables*).

Specifically, the probability dW of finding a particle inside an infinitesimal volume $dV \equiv d^3r$ is proportional to this volume and may be characterized by the *probability density* $w \equiv dW/d^3r$ that in turn is related to the wavefunction as

$$w = |\Psi(\mathbf{r}, t)|^2 \equiv \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t), \quad (1.22a)$$

where sign * means the complex conjugate. As a result, the total probability of finding the particle somewhere inside a volume V may be calculated as

$$W = \int_V w d^3r = \int_V \Psi^* \Psi d^3r. \quad (1.22b)$$

In particular, if the volume V contains the particle *definitely* (i.e. with the 100% probability, $W = 1$), Eq. (22b) is reduced to the so-called *normalization condition*

$$\int_V \Psi^* \Psi d^3r = 1. \quad (1.22c)$$

(ii) Observables and operators. To each observable A , quantum mechanics associates a certain *linear operator* $\hat{A}$, such that, in the perfect conditions mentioned above, the average measured value (also called the *expectation value*) of A is expressed as²⁵

$$\langle A \rangle = \int_V \Psi^* \hat{A} \Psi d^3r, \quad (1.23)$$

where $\langle \dots \rangle$ means the statistical average, i.e. the result of averaging the measurement results over a large *ensemble* (set) of macroscopically similar experiments, and Ψ is the normalized wavefunction – see Eq. (22c). For Eqs. (22) and (23) to be compatible, the *identity* (“unit”) operator $\hat{I}$, defined by relation

$$\hat{I}\Psi = \Psi, \quad (1.24)$$

has to be associated with a particular type of measurement, namely with particle's detection.

(iii) Hamiltonian operator and the Schrödinger equation. Another particular operator, the *Hamiltonian* $\hat{H}$, whose observable is the particle's energy E , also plays in wave mechanics a very special role, because it participates in the *Schrödinger equation*,

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi, \quad (1.25)$$

²⁴ This is one more important caveat. As we will see in Chapter 7, in many cases even the Hamiltonian particles cannot be described by a certain wavefunction, and allow only a more general (and less precise) description, e.g., by the *density matrix*.

²⁵ This key measurement postulate is sometimes called the *Born rule*.

that determines wavefunction's dynamics, i.e. its time evolution.

(iv) Radius-vector and momentum operators. In the coordinate representation accepted in wave mechanics, the (vector) operator of particle's radius-vector $\mathbf{r}$ just multiplies the wavefunction by this vector, while the operator of particle's momentum²⁶ is represented by the spatial derivative:

Operators of
coordinate and
momentum

$$\hat{\mathbf{p}} = -i\hbar\nabla, \quad (1.26a)$$

where ∇ is the *del* (or “nabla”) vector operator.²⁷ Thus in the Cartesian coordinates,

$$\hat{\mathbf{r}} = \mathbf{r} = \{x, y, z\}, \quad \hat{\mathbf{p}} = -i\hbar\left\{\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right\}. \quad (1.26b)$$

(v) Correspondence principle. In the limit when quantum effects are insignificant, e.g., when the characteristic scale of action S ²⁸ (i.e. the product of the relevant energy and time scales of the problem) is much larger than Planck's constant $\hbar$, all wave mechanics results have to tend to those given by classical mechanics. Mathematically, the correspondence is achieved by duplicating the classical relations between observables by similar relations between the corresponding operators. For example, for a free particle, the Hamiltonian (that in this case corresponds to the kinetic energy alone) has the form

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \quad (1.27a)$$

Free
particle's
Hamiltonian

so that, taking into account Eq. (26b), in the Cartesian coordinates,

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right). \quad (1.27b)$$

Even before a discussion of physics of the postulates (offered in the next section), we may immediately see that they indeed provide a way toward the resolution of the apparent contradiction between the wave and corpuscular properties of particles. For a free particle, the Schrödinger equation (25), with the substitution of Eq. (27), takes the form

Free
particle's
Schrödinger
equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi, \quad (1.28)$$

whose particular (but most important) solution is a plane, monochromatic wave,²⁹

Plane
wave
solution

$$\Psi(\mathbf{r}, t) = ae^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \quad (1.29)$$

²⁶ For an electrically charged particle in magnetic field, this relation is valid for its *canonical* momentum – see Sec. 3.1 below.

²⁷ See, e.g., Secs. 8-10 of the *Selected Mathematical Formulas* appendix (below, referred to as MA). Note that according to these formulas, the del operator follows all the geometric rules of the usual (*c*-number) vectors. This is, by definition, true for other vector operators of quantum mechanics to be discussed below.

²⁸ See, e.g., CM Sec. 10.3.

²⁹ See, e.g., CM Sec. 7.7 and/or EM Sec. 7.1.

where a , $\mathbf{k}$ and ω are constants. Indeed, plugging Eq. (29) into Eq. (28), we immediately see the plane wave, with an arbitrary amplitude a , is indeed a solution of the Schrödinger equation, provided a specific *dispersion relation* between wavevector $\mathbf{k}$ and frequency ω :

$$\hbar\omega = \frac{(\hbar k)^2}{2m}. \quad (1.30)$$

Free
particle's
dispersion
relation

Constant a may be calculated, for example, assuming that solution (29) is extended over a certain volume V , while beyond it, $\Psi = 0$. Then from the normalization condition (22c) and Eq. (29), we get³⁰

$$|a|^2 V = 1. \quad (1.31)$$

Now we can use Eqs. (23), (26) and (27) to calculate the expectation value of particle's momentum $\mathbf{p}$ and energy E (which, for a free particle, coincides with its Hamiltonian function H). The result is

$$\langle \mathbf{p} \rangle = \hbar \mathbf{k}, \quad \langle E \rangle = \langle H \rangle = \frac{(\hbar k)^2}{2m}; \quad (1.32)$$

according to Eq. (30), the last equality may be rewritten as $\langle E \rangle = \hbar\omega$.

Next, Eq. (23) enables one to calculate not only the statistical average (in the math speak, the *first moment*) of an observable, but also its higher moments, notably the *second moment* (in physics, usually called either the *variance* or *dispersion*):

$$\langle \tilde{A}^2 \rangle \equiv \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2, \quad (1.33)$$

Observable's
variance

and hence its *root mean square (r.m.s.) fluctuation*,

$$\delta A \equiv \langle \tilde{A}^2 \rangle^{1/2}, \quad (1.34)$$

Observable's
uncertainty

that characterizes the scale of deviations $\tilde{A} \equiv A - \langle A \rangle$ of measurement results from the average, i.e. the *uncertainty* of observable A . In application to wavefunction (29), these relations yield $\delta E = 0$, $\delta \mathbf{p} = 0$, while the particle coordinate $\mathbf{r}$ (at $V \rightarrow \infty$) is completely uncertain. This means that in the plane-wave, monochromatic state (29), the energy and momentum of the particle are *exactly* defined, so that the signs of statistical average in Eqs. (32) might be removed. Thus, these relations are reduced to the experimentally-inferred Eqs. (5) and (15), though the relation of frequency ω of wavefunction's evolution in time to experimental observations still has to be clarified.

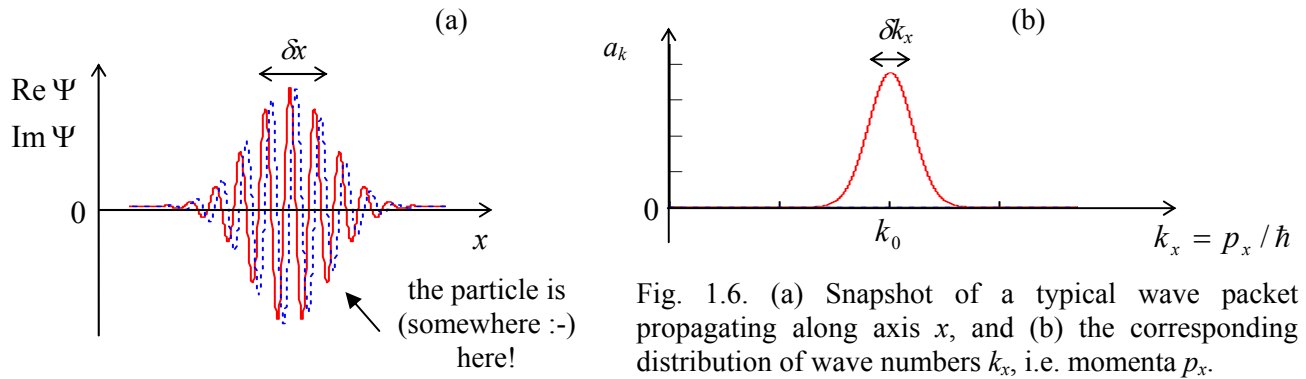
Hence the wave mechanics postulates may indeed explain the observed wave properties of nonrelativistic particles. (For photons, we would need a relativistic formalism – see Ch. 9 below.) On the other hand, due to the linearity of the Schrödinger equation (25), any sum of its solutions is also a solution – the so-called *linear superposition principle*. For a free particle, this means that a set of plane waves (29) is also a solution of this equation. Such sets, with close values of $\mathbf{k}$ and hence $\mathbf{p} = \hbar \mathbf{k}$ (and, according to Eq. (30), of ω as well), may be used to describe spatially localized “pulses”, called *wave packets* — see Fig. 6. In Sec. 2.1, I will prove (or rather reproduce H. Weyl's proof :-)) that the wave

³⁰ For infinite space ($V \rightarrow \infty$), Eq. (31) yields $a \rightarrow 0$, i.e. wavefunction (29) vanishes. This formal problem may be readily resolved considering sufficiently long wave packets – see Sec. 2.2 below.

packet extension δx in any direction (say, x) is related to the width δk_x of the corresponding component of its wave vector distribution as $\delta x \delta k_x \geq 1/2$, and hence, according to Eq. (15), to the width δp_x of the momentum component distribution as

$$\delta x \cdot \delta p_x \geq \frac{\hbar}{2}. \quad (1.35)$$

Heisenberg's
uncertainty
relation



This is the famous the famous *Heisenberg's uncertainty principle*, which quantifies the first postulate's point that coordinate and momentum cannot be defined exactly simultaneously. However, since the Planck's constant is extremely small on the human scale of things, it still allows for the particle's localization in a very small volume even if the momentum spread in the wave packet is also small on that scale. For example, according to Eq. (35), a 0.1% spread of momentum of a 1 keV electron ($p \sim 1.7 \times 10^{-24}$ kg·m/s) allows a wave packet to be as small as $\sim 3 \times 10^{-10}$ m. (For a heavier particle such as a proton, the packet would be even tighter.) As a result, wave packets may be used to describe particles that are point-like from the macroscopic point of view.

In a nutshell, this is the main idea of the wave mechanics, and the first part of this course (Chapters 1-3) will be essentially a discussion of various manifestations of this approach. During this discussion, we will not only evidence wave mechanics' many triumphs within its applicability domain, but will also gradually accumulate evidence for its handicaps, which force the eventual transfer to a more general formalism – to be discussed in Chapter 4 and beyond.

1.3. Postulates' discussion

The postulates listed in the previous section look very simple, and they are hopefully familiar to the reader from his or her undergraduate studies. However, the physics of these axioms are very deep, they lead to several counter-intuitive conclusions, and their in-depth discussion requires solutions of several key problems using these axioms. This is why in this section I will give only an initial, admittedly superficial discussion of the postulates, and will be repeatedly returning to the conceptual foundations of quantum mechanics throughout the course, especially in Secs. 7.7, 10.1, and 10.2.

First of all, the fundamental uncertainty of observables, which is in the core of postulate (i), is very foreign to the basic ideas of classical mechanics, and historically has made quantum mechanics so hard to swallow for many star physicists, notably including A. Einstein – despite his 1905 work which essentially launched the whole field! However, this fact has been confirmed by numerous experiments,

and (more importantly) there have not been a single confirmed experiment which would contradict to this postulate, so that quantum mechanics was long ago promoted from a theoretical hypothesis to the rank of a reliable scientific theory.

One more remark in this context is that Eq. (25) itself is *deterministic*, i.e. conceptually enables an *exact* calculation of wavefunction's distribution in space at any instant t , provided that its initial distribution, and particle's Hamiltonian, are known exactly. In classical kinetics, the probability density distribution $w(\mathbf{r}, t)$ may be also calculated from deterministic differential equations, e.g., the Fokker-Planck equation or the Boltzmann equation.³¹ The quantum-mechanical description differs from those situations in two important aspects. First, in the perfect conditions outlined above (exact initial state preparation, no irreversible interaction with environment, the best possible measurement), the Fokker-Planck equation reduces to the 2nd Newton law, i.e. the statistical uncertainty disappears. In quantum mechanics this is not true: the quantum uncertainty, such as Eq. (35), persists even in this limit. Second, the wavefunction $\Psi(\mathbf{r}, t)$ gives more information than just $w(\mathbf{r}, t)$, because besides the modulus of Ψ , involved in Eq. (22), this complex function also has *phase* $\varphi \equiv \arg \Psi$, and may affect some observables, describing, in particular, the interference and diffraction of the de Broglie waves.

Next, it is very important to understand that the relation between the quantum mechanics to experiment, given by postulate (ii), necessarily involves another key notion: that of the corresponding *statistical ensemble*. Such ensemble may be defined as a set of many experiments carried out at apparently (*macroscopically*) similar conditions, which nevertheless may lead to different measurement results (*outcomes*). Indeed, the probability of a certain (n -th) outcome of an experiment may be only defined for a certain ensemble, as the limit

$$W_n \equiv \lim_{M \rightarrow \infty} \frac{M_n}{M}, \quad \text{with } M \equiv \sum_{n=1}^N M_n, \quad (1.36)$$

Definition
of
probability

where M is the total number of experiments, M_n is the number of outcomes of the n -th type, and N is the number of different outcomes. It is clear that a particular choice of an ensemble may affect probabilities W_n very significantly.

For example, if we pull out playing cards at random from a pack of 52 different cards of 4 suits, the probability W_n of getting a certain card (e.g., the queen of spades) is $1/52$. However, if cards of a certain suit (say, hearts) had been taken out from the pack in advance, the probability of getting the queen of spades is higher, $1/39$. It is important that we would also get the last number for probability even if we had used the full 52-card pack, but by some reason ignored results of all experiments giving us any rank of hearts.

Similarly, in quantum mechanics, the probability distributions (and hence expectation values of particle coordinate and other observables) depend not only on the experiment setup, but also on the set of outcomes we count. Because of the fundamental relation (22) between w and Ψ , this means the wavefunction also depends on those factors, i.e. on both the experiment set preparation *and* the subset of outcomes taken into account. The insistence on the attribution of the wavefunction to a single experiment, both before and after the measurement, may lead to very unphysical interpretations of some experiments, including wavefunction's evolution not described by the Schrödinger equation (the so-called *wave packet reduction*), subluminal action on distance, etc. Later in the course we will see that minding the statistical nature of the quantum mechanics, and in particular the dependence of the

³¹ See, e.g., SM Secs. 5.8 and 6.2, respectively.

wavefunction on statistical ensemble's specification, may readily explain some apparent paradoxes of quantum measurements.

Let me also emphasize that statistics is intimately related to the information theory - and not only via their common mathematical background, the probability theory. For example, the question, "What subset of experimental results we will count?" may be replaced by the question, "What subset of results will we use information about?" As a result, the reader has to be prepared to the use of information theory notions for the discussion quantum mechanics, or at least its relation to experiment - i.e. to the "physical reality". This feature of quantum mechanics makes some physicists uncomfortable, because much of classical mechanics and electrodynamics may be discussed without any reference to information. In quantum mechanics (as in statistical mechanics), such an abstraction is impossible.

Proceeding to postulate (ii) and in particular Eq. (23), a better feeling of this definition may be obtained by its comparison with the general definition of the expectation value (i.e. the statistical average) in the probability theory. Namely, let each of N possible outcomes in a set of M macroscopically similar experiments give a certain value A_n of observable A ; then

Definition
of statistical
average

$$\langle A \rangle \equiv \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{n=1}^N A_n M_n = \sum_{n=1}^N A_n W_n. \quad (1.37)$$

Taking into account Eq. (22), which relates W and Ψ , the structure of Eq. (23) and the final form of Eq. (37) is similar. Their exact relation will be further discussed in Sec. 4.1.

1.4. Continuity equation

The wave mechanics postulates survive one more sanity check: they satisfy the natural requirement that the particle does not appear or vanish in the course of the quantum evolution.³² Indeed, let us use Eq. (22) to calculate the rate of change of the probability W to find the particle within a certain volume V :

$$\frac{dW}{dt} = \frac{d}{dt} \int_V \Psi \Psi^* d^3r. \quad (1.38)$$

Assuming for simplicity that the boundaries of volume V do not move, it is sufficient to carry out the partial differentiation of the product $\Psi \Psi^*$ inside the integral. Using the time-dependent Schrödinger equation (25), together with its complex conjugate,

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = (\hat{H}\Psi)^*, \quad (1.39)$$

we get

$$\frac{dW}{dt} = \int_V \frac{\partial}{\partial t} (\Psi \Psi^*) d^3r = \int_V \left(\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right) d^3r = \frac{1}{i\hbar} \int_V \left[\Psi^* (\hat{H}\Psi) - \Psi (\hat{H}\Psi)^* \right] d^3r. \quad (1.40)$$

³² Note that this requirement is not extended to the relativistic quantum theory – see Chapter 9 below.

Let the particle move in a field of external forces (not necessarily constant in time), so that its classical Hamiltonian function H is a sum of particle's kinetic energy $p^2/2m$ and its potential energy $U(\mathbf{r}, t)$.³³ According to the correspondence principle, the Hamiltonian operator may be presented as the sum³⁴

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}, t). \quad (1.41)$$

Hamiltonian
of a particle
in a field

At this stage we should notice that such operator, when acting on a real function, returns a real function.³⁵ Hence, the result of its action on an arbitrary complex function $\Psi = a + ib$ (where a and b are real) is

$$\hat{H}\Psi = \hat{H}(a + ib) = \hat{H}a + i\hat{H}b, \quad (1.42)$$

where $\hat{H}a$ and $\hat{H}b$ are also real, while

$$(\hat{H}\Psi)^* = (\hat{H}a + i\hat{H}b)^* = \hat{H}a - i\hat{H}b = \hat{H}(a - ib) = \hat{H}\Psi^*. \quad (1.43)$$

This means that Eq. (40) may be rewritten as

$$\frac{dW}{dt} = \frac{1}{i\hbar} \int_V [\Psi^* \hat{H}\Psi - \Psi \hat{H}\Psi^*] d^3r = -\frac{\hbar^2}{2m} \frac{1}{i\hbar} \int_V [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] d^3r. \quad (1.44)$$

Now, let us use general rules of vector calculus³⁶ to write the following identity:

$$\nabla \cdot (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) = \Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*, \quad (1.45)$$

A comparison of Eqs. (44) and (45) shows that we may write

$$\frac{dW}{dt} = - \int_V (\nabla \cdot \mathbf{j}) d^3r, \quad (1.46)$$

where vector $\mathbf{j}$ is defined as

$$\mathbf{j} \equiv \frac{i\hbar}{2m} (\Psi \nabla \Psi^* - \text{c.c.}) = \frac{\hbar}{m} \text{Im}(\Psi^* \nabla \Psi), \quad (1.47)$$

Probability
current
density

where c.c. means the complex conjugate of the previous expression – in this case, $(\Psi \nabla \Psi^*)^*$, i.e. $\Psi^* \nabla \Psi$. Now using the well-known divergence theorem,³⁷ Eq. (46) may be rewritten as the *continuity equation*

$$\frac{dW}{dt} + I = 0, \quad \text{with } I \equiv \int_S j_n d^2r, \quad (1.48)$$

Continuity
equation:
integral
form

³³ As a reminder, such description is valid not only for potential forces (in that case U has to be time-independent), but also for any force $\mathbf{F}(\mathbf{r}, t)$ which may be presented via the gradient of $U(\mathbf{r}, t)$ – see, e.g., CM Chapters 2 and 10. (A good example when such a description is *impossible* is given by the magnetic component of the Lorentz force – see, e.g., EM Sec. 9.7, and also Sec. 3.1 of this course.)

³⁴ Historically, this was the main step made (in 1926) by E. Schrödinger on the background of L. de Broglie's idea. The probabilistic interpretation of the wavefunction was put forward, almost simultaneously, by M. Born.

³⁵ In Chapter 4, we will discuss a more general family of *Hermitian operators*, which have this property.

³⁶ See, e.g., MA Eq. (11.4a), combined with the del operator's definition $\nabla^2 \equiv \nabla \cdot \nabla$.

³⁷ See, e.g., MA Eq. (12.2).

where j_n is the projection of vector $\mathbf{j}$ on the outwardly directed normal to surface S that limits volume V , i.e. the scalar product $\mathbf{j} \cdot \mathbf{n}$, where $\mathbf{n}$ is the unit vector along this normal.

Equations (47) and (48) show that if the wavefunction on the surface vanishes, the total probability W of finding the particle within the volume does not change, providing the required sanity check. In the general case, Eq. (48) says that dW/dt equals to flux I of vector $\mathbf{j}$ through the surface, with the minus sign. It is clear that this vector may be interpreted as the *probability current density* - and I , as the total *probability current* through surface S . This interpretation may be further supported by rewriting Eq. (47) for a wavefunction presented in the polar form $\Psi = ae^{i\varphi}$, with real a and φ :

$$\mathbf{j} = a^2 \frac{\hbar}{m} \nabla \varphi, \quad (1.49)$$

- evidently a real quantity. Note that for a real wavefunction, or even for that with an arbitrary but space-constant phase φ , the probability current density vanishes. On the contrary, for the traveling wave (29), with a constant probability density $w = a^2$, Eq. (49) yields a nonvanishing (and physically very transparent) result:

$$\mathbf{j} = w \frac{\hbar}{m} \mathbf{k} = w \frac{\mathbf{p}}{m} = w \mathbf{v}, \quad (1.50)$$

where $\mathbf{v} = \mathbf{p}/m$ is particle's velocity. If multiplied by the particle's mass m , the probability density w turns into the (average) mass density ρ , and the probability current density into the *mass flux density* $\rho \mathbf{v}$, while if multiplied by the total electric charge q of the particle, with w turning into the *charge density* σ , $\mathbf{j}$ becomes the electric current density, both satisfying the classical continuity equations similar to Eq. (48).³⁸

Finally, let us recast the continuity equation, rewriting Eq. (46) as

$$\int_V \left(\frac{\partial w}{\partial t} + \nabla \cdot \mathbf{j} \right) d^3r = 0. \quad (1.51)$$

Now we may argue that this equality may be true for any choice of volume V only if the expression under the integral vanishes everywhere, i.e. if

Continuity
equation:
differential
form

$$\frac{\partial w}{\partial t} + \nabla \cdot \mathbf{j} = 0. \quad (1.52)$$

This *differential form* of the continuity equation is sometimes more convenient than its *integral form* (48).

1.5. Eigenstates and eigenvalues

Now let us discuss important corollaries of wave mechanics' *linearity*. First of all, it uses only *linear operators*. This term means that the operators must obey the following two rules:³⁹

³⁸ See, e.g., respectively, CM 7.2 and EM Sec. 4.1.

³⁹ By the way, if any equality involving operators is valid for an arbitrary wavefunction, the latter is frequently dropped from notation, resulting in an *operator equality*. In particular, Eq. (53) may be readily used to prove that the operators are *commutative*: $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$, and *associative*: $(\hat{A}_1 + \hat{A}_2) + \hat{A}_3 = \hat{A}_1 + (\hat{A}_2 + \hat{A}_3)$.

$$(\hat{A}_1 + \hat{A}_2)\Psi = \hat{A}_1\Psi + \hat{A}_2\Psi, \quad (1.53)$$

$$\hat{A}(c_1\Psi_1 + c_2\Psi_2) = \hat{A}(c_1\Psi_1) + \hat{A}(c_2\Psi_2) = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2, \quad (1.54)$$

where Ψ_n are arbitrary wavefunctions, while c_n are arbitrary constants (in quantum mechanics, frequently called *c-numbers*, to distinguish them from operators and wavefunctions). Most important examples of linear operators are given by:

- (i) the multiplication by a function, such as for operator $\hat{\mathbf{r}}$ in wave mechanics, and
- (ii) the spatial or temporal differentiation of the wavefunction, such as in Eqs. (25)-(27).

Next, it is of key importance that the Schrödinger equation (25) is also linear. (We have already used this fact when we discussed wave packets in the last section.) This means that if each of functions Ψ_n are (particular) solutions of Eq. (25) with a certain Hamiltonian, then an arbitrary linear combination

$$\Psi = \sum_n c_n \Psi_n \quad (1.55)$$

is also a solution of the same equation.⁴⁰

Now let us use the linearity of wave mechanics to accomplish an apparently impossible feat: immediately find the *general* solution to the Schrödinger equation for the most important case when system's Hamiltonian does not depend on time explicitly – for example, like in Eq. (27), or in Eq. (41) with time-independent $U = U(\mathbf{r})$. First of all, let us prove that the following product,

$$\Psi_n = T_n(t)\psi_n(\mathbf{r}), \quad (1.56)$$

Variable
separation

qualifies as a (particular) solution to the Schrödinger equation. Indeed, plugging Eq. (56) into Eq. (25), using the fact that for a time-independent Hamiltonian

$$\hat{H}T_n(t)\psi_n(\mathbf{r}) = T_n(t)\hat{H}\psi_n(\mathbf{r}), \quad (1.57)$$

and dividing both parts of the equation by $\Psi_n = T_n\psi_n$, we get

$$\frac{i\hbar\dot{T}_n}{T_n} = \frac{\hat{H}\psi_n}{\psi_n}, \quad (1.58)$$

where (here and below) the dot denotes the differentiation over time. The left hand side of this equation may depend only on time, while the right hand one, only on coordinates. These facts may be only reconciled if we assume that each of these parts is equal to (the same) constant of the dimension of energy, which I will denote as E_n .⁴¹ As a result, we are getting two separate equations for the temporal and spatial parts of the wavefunction:

$$i\hbar\dot{T}_n = E_n T_n, \quad (1.59)$$

⁴⁰ It may seem strange that the *linear* Schrödinger equation correctly describes quantum properties of systems whose classical dynamics is described by *nonlinear* equations of motion (e.g., an anharmonic oscillator – see, e.g., CM Sec. 4.2). Note, however, that equations of classical physical kinetics (see, e.g., SM Chapter 6) also have this property, so it is not specific to quantum mechanics.

⁴¹ This argumentation, leading to *variable separation*, is very common in mathematical physics – see, e.g., its discussion in EM Sec. 2.5.

Stationary
Schrödinger
equation

$$\hat{H}\psi_n = E_n\psi_n. \quad (1.60)$$

The first of these equations is readily integrable, giving

Stationary
state:
time
evolution

$$T_n = \text{const} \times \exp\{-i\omega_n t\}, \quad \text{with } \omega_n \equiv \frac{E_n}{\hbar}, \quad (1.61)$$

and thus substantiating the fundamental relation (5) between energy and frequency. Plugging Eqs. (56) and (61) into Eq. (22), we see that in such a state, the probability w of finding the particle at a certain location does not depend on time. Doing the same with Eq. (23) shows that the same is true for the expectation value of any operator that does not depend on time explicitly:

$$\langle A \rangle_n \equiv \int \psi_n^* \hat{A} \psi_n d^3r = \text{const}. \quad (1.62)$$

Due to this property, the states described by Eqs. (56), (60), and (61), are called *stationary*. In contrast to the simple and universal time dependence (61), the spatial distributions $\psi_n(\mathbf{r})$ of the stationary states are often hard to find, and the solution of the *stationary* (or “time-independent”) *Schrödinger equation* (60),⁴² which describes the distributions, for various situations is a major focus of wave mechanics.

The stationary Schrödinger equation (60), with time-independent Hamiltonian (41),

Stationary
Schrödinger
equation
for static
potential

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + U(\mathbf{r})\psi_n = E_n\psi_n, \quad (1.63)$$

falls into the mathematical category of linear *eigenproblems*,⁴³ in which *eigenfunctions* ψ_n and *eigenvalues* E_n should be found simultaneously - self-consistently.⁴⁴ Mathematics tells us that for the such problems with space-confined eigenfunctions ψ_n , tending to zero at $r \rightarrow \infty$, the spectrum of eigenvalues is *discrete*. It also proves that the eigenfunctions corresponding to different eigenvalues are *orthogonal*, i.e. that space integrals of the products $\psi_n \psi_{n'}^*$ vanish for all pairs with $n \neq n'$. Moreover, due to the Schrödinger equation linearity, each of these functions may be multiplied by a constant coefficient to make this set *orthonormal*:

$$\int \psi_n^* \psi_{n'} d^3r = \delta_{n,n'} \equiv \begin{cases} 1, & \text{if } n = n', \\ 0, & \text{if } n \neq n'. \end{cases} \quad (1.64)$$

Also, the eigenfunctions form a *full set*, meaning that an arbitrary function $\psi(\mathbf{r})$, in particular the actual wavefunction Ψ of the system in the initial moment of its evolution (which I will take for $t = 0$, with a few exceptions), may be presented as a unique expansion over the eigenfunction set:

$$\Psi(\mathbf{r}, 0) = \sum_n c_n \psi_n(\mathbf{r}). \quad (1.65)$$

The expansion coefficients c_k may be readily found by multiplying both parts of Eq. (65) by ψ_n^* , integrating the result over the space, and using Eq. (64). The result is

⁴² In contrast, the initial Eq. (24) is frequently called the *time-dependent* or *nonstationary Schrödinger equation*.

⁴³ From German root *eigen* meaning “particular” or “characteristic”.

⁴⁴ Eigenvalues of energy are frequently called *eigenenergies*, and it is often said that eigenfunction ψ_n and *eigenenergy* E_n together characterize n -th *stationary eigenstate* of the system.

$$c_n = \int \psi_n^*(\mathbf{r}) \Psi(\mathbf{r}, 0) d^3r. \quad (1.66)$$

Now let us consider the following wavefunction

$$\Psi(\mathbf{r}, t) = \sum_n c_n a_k(t) \psi_k(\mathbf{r}) = \sum_n c_n \psi_n(\mathbf{r}) \exp\left\{-i \frac{E_n}{\hbar} t\right\}. \quad (1.67)$$

Since each term of the sum has the form (56) and satisfies the Schrödinger equation, so does the sum as the whole. Moreover, if coefficients c_n are derived in accordance with Eq. (66), then solution (67) satisfies the initial conditions as well. At this moment we can again use one more help by mathematicians who tell us that the partial differential equation of type (28) with the Hamiltonian operator (41) with fixed initial conditions, may have only one (*unique*) solution. This means that in our case of motion in a time-independent potential $U = U(\mathbf{r})$, Eq. (67) gives the *general* solution of the time-dependent Schrödinger equation (25) for our case:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(\mathbf{r}) \Psi. \quad (1.68)$$

We will repeatedly use this key fact through the course, though in many cases, following the physical sense of particular problems, will be more interested in certain specific particular solutions of Eq. (68) rather in the whole linear superposition (67).

In order to get some feeling of functions ψ_n , let us consider perhaps the simplest example, which nevertheless will be the basis for discussion of many less trivial problems: a particle confined in a *rectangular quantum well*⁴⁵ with a flat “bottom” and sharp and infinitely high “hard walls”:

$$U(\mathbf{r}) = \begin{cases} 0, & \text{for } 0 < x < a_x, \quad 0 < y < a_y, \quad \text{and } 0 < z < a_z, \\ +\infty, & \text{otherwise.} \end{cases} \quad (1.69)$$

The only way to keep the product $U\psi_n$ in Eq. (68) finite outside the well, is to have $\psi = 0$ in these regions. Also, the function have to be continuous everywhere, to avoid the divergence of its Laplace operator. Hence, we may solve the stationary Schrödinger equation (63) only inside the well, where it takes a simple form⁴⁶

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n = E_n \psi_n, \quad (1.70a)$$

with zero boundary conditions on all the walls. For our particular geometry, it is natural to express the Laplace operator in the Cartesian coordinates $\{x, y, z\}$ aligned with the well sides, so that we get the following *boundary problem*:

⁴⁵ By using the term “quantum well” for what is essentially a *potential well* I bow to a common, but a very unfortunate convention. Indeed, this term seems to imply that the particle’s confinement in such a “quantum well” is a phenomenon specific for quantum mechanics, while as we will repeatedly see in this course, that the opposite is true: quantum effects do as much as they only can to overcome particle’s confinement in a potential well, letting the particle to partly penetrate in the “classically forbidden” regions.

⁴⁶ Rewritten as $\nabla^2 f + k^2 f = 0$, this is the *Helmholtz equation*, which describes scalar waves of any nature (with wave vector $\mathbf{k}$) in a uniform, linear media – see, e.g., CM Sec. 5.5 and/or EM Secs. 7.7-7.9.

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n = E_n \psi_n, \quad \text{for } 0 < x < a_x, \quad 0 < y < a_y, \quad \text{and } 0 < z < a_z, \quad (1.70b)$$

$$\psi_n = 0, \quad \text{for } x = 0 \text{ and } a_x; \quad y = 0 \text{ and } a_y; \quad z = 0 \text{ and } a_z.$$

This problem may be readily solved using the same variable separation method which was used earlier in this section to separate the spatial and temporal variables, now to separate Cartesian spatial variables from each other. Let us look for a particular solution in the form

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z). \quad (1.71)$$

(It is convenient to postpone taking care of proper indices for a minute.) Plugging this expression into the Eq. (70b) and dividing by $\psi = XYZ$, we get

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} \right) = E. \quad (1.72)$$

Now let us repeat the standard argumentation of the variable separation method: since each term in the parentheses may be only a function of the corresponding argument, the equality is possible only if each term is a constant - with the dimensionality of energy. Calling them E_x , etc., we get three 1D equations

$$-\frac{\hbar^2}{2m} \frac{1}{X} \frac{d^2 X}{dx^2} = E_x, \quad -\frac{\hbar^2}{2m} \frac{1}{Y} \frac{d^2 Y}{dy^2} = E_y, \quad -\frac{\hbar^2}{2m} \frac{1}{Z} \frac{d^2 Z}{dz^2} = E_z, \quad (1.73)$$

with Eq. (72) turning into the energy-matching condition

$$E_x + E_y + E_z = E. \quad (1.74)$$

All three ordinary differential equations (73), and their solutions, are similar. For example, for $X(x)$, we have a 1D Helmholtz equation

$$\frac{d^2 X}{dx^2} + k_x^2 X = 0, \quad \text{with } k_x^2 \equiv \frac{2mE_x}{\hbar^2}, \quad (1.75)$$

and simple boundary conditions: $X(0) = X(a_x) = 0$. Let me hope that the reader knows how to solve this well-known 1D boundary problem - describing, for example, usual mechanical waves on a guitar string, though with a very much different expression for k_x . The problem allows an infinite number of sinusoidal standing-wave solutions,⁴⁷

$$X = \left(\frac{2}{a_x} \right)^{1/2} \sin k_x x = \left(\frac{2}{a_x} \right)^{1/2} \sin \frac{\pi n_x x}{a_x}, \quad \text{with } n_x = 1, 2, \dots, \quad (1.76)$$

corresponding to eigenenergies

$$E_x = \frac{\hbar^2}{2m} k_x^2 = \frac{\pi^2 \hbar^2}{2m a_x^2} n_x^2 \equiv E_{x1} n_x^2. \quad (1.77)$$

⁴⁷ The front coefficient is selected in a way that ensures the (ortho)normality condition (64).

Figure 7 shows this result using a somewhat odd but very graphic and hence common way when the eigenenergy values (frequently called *energy levels*) are used as horizontal axes for plotting eigenfunctions, despite their different dimensionality.

Due to the similarity of all Eqs. (73), $Y(y)$ and $Z(z)$ are similar functions of their arguments, and may also be numbered by integers (say, n_y and n_z) independent of n_x , so that the spectrum of the total energy (74) is

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right). \quad (1.78)$$

Rectangular
quantum well:
energy levels

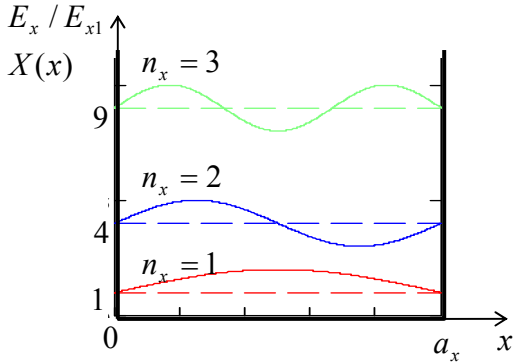


Fig. 1.7. Eigenfunctions (solid lines) and eigenvalues (dashed lines) of the 1D wave equation (75) on a finite-length segment. Solid black lines show the potential energy profile of the problem.

Thus, in this 3D problem, the role of index n in Eq. (67) is played by a set of 3 independent integers $\{n_x, n_y, n_z\}$. In quantum mechanics, such integers play a key role, and thus have a special name, *quantum numbers*. Now the general solution (67) of our simple problem may be presented as the sum

$$\Psi(\mathbf{r}, t) = \sum_{n_x, n_y, n_z=1}^{\infty} c_{n_x, n_y, n_z} \sin \frac{\pi n_x x}{a_x} \sin \frac{\pi n_y y}{a_y} \sin \frac{\pi n_z z}{a_z} \exp \left\{ -i \frac{E_{n_x, n_y, n_z}}{\hbar} t \right\}, \quad (1.79)$$

Rectangular
quantum
well:
general
solution

with the coefficients which may be readily calculated from the initial wavefunction $\Psi(\mathbf{r}, 0)$, using Eq. (66), again with the replacement $n \rightarrow \{n_x, n_y, n_z\}$. This simplest problem is a good illustration of the basic features of wave mechanics for a spatially-confined motion, including the discrete energy spectrum, and (in this case, evidently) orthogonal eigenfunctions.

An example of the opposite limit of a *continuous spectrum* for *unconfined motion* of a free particle is given by plane waves (29) which, with the account of relations $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$, may be viewed as the product of the time-dependent factor (46) by eigenfunction

$$\psi_{\mathbf{k}} = a_{\mathbf{k}} \exp\{i\mathbf{k} \cdot \mathbf{r}\} \quad (1.80)$$

Free
particle:
eigen-
functions

that is the solution to the stationary Schrödinger equation (70a) if it is valid in the whole space.⁴⁸

The reader should not be worried too much by the fact that the fundamental solution (80) in free space is a *traveling* wave (having, in particular, nonvanishing value (50) of the probability current $\mathbf{j}$),

⁴⁸ In some systems (e.g., a particle interacting with a finite-depth quantum well), a discrete energy spectrum within a certain interval of energies may coexist with a continuous spectrum in a complementary interval. However, the conceptual philosophy of eigenfunctions and eigenvalues remains the same in this case as well.

while those inside a quantum well are *standing* waves, with $\mathbf{j} = 0$, even though the free space may be legitimately considered as the ultimate limit of a quantum well with volume $V = a_x a_y a_z \rightarrow \infty$. Indeed, due to the linearity of wave mechanics, two traveling-wave solutions (80) with equal and opposite values of momentum (and hence with the same energy) may be readily combined to give a standing-wave solution, for example $\exp\{i\mathbf{k}\cdot\mathbf{r}\} + \exp\{-i\mathbf{k}\cdot\mathbf{r}\} = 2\cos(\mathbf{k}\cdot\mathbf{r})$, with the net current $\mathbf{j} = 0$. Thus, depending on convenience for solution of a particular problem, we can present the general solution as a sum of either traveling-wave or standing-wave eigenfunctions.

Since in the free space there are no boundary conditions to satisfy, Cartesian components of the wave vector $\mathbf{k}$ in Eq. (80) can take any real values. (This is why it is more convenient to label the wavefunctions and eigenenergies,

Free
particle:
eigen-
energies

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \geq 0, \quad (1.81)$$

by their wave vector $\mathbf{k}$ rather than an integer index.) However, one aspect of systems with continuous spectrum requires a bit more math caution: summation (67) should be replaced by integration over a continuous index or indices (in this case, 3 components of vector $\mathbf{k}$). The main rule of such replacement may be readily extracted from Eq. (76): according to this relation, for standing-wave solutions, the eigenvalues of k_x are *equidistant*, i.e. separated by equal intervals $\Delta k_x = \pi/a_x$ (with the similar relations for other two Cartesian components of vector $\mathbf{k}$). Hence the number of different eigenvalues of the standing wave vector $\mathbf{k}$ (with $k_x, k_y, k_z \geq 0$), within a volume $d^3k \gg 1/V$ of the $\mathbf{k}$ space is just $dN = d^3k/(\Delta k_x \Delta k_y \Delta k_z) = V/\pi^3$. Since in continuum it is more convenient to work with traveling waves, we should take into account that, as was just discussed, there are two different traveling wave vectors ($\mathbf{k}$ and $\mathbf{k}' = -\mathbf{k}$) corresponding to each standing wave vector $\mathbf{k}$. Hence the same number of physically different states corresponds to $2^3 = 8$ -fold larger $\mathbf{k}$ space (which now is infinite in all directions) or, equivalently, to a smaller number of states per unit volume d^3k :

3D
number
of states

$$dN = \frac{V}{(2\pi)^3} d^3k. \quad (1.82)$$

For $dN \gg 1$, this expression is independent on the boundary conditions,⁴⁹ and is frequently presented as the following *summation rule*

Summation
over
3D states

$$\lim_{k^3 V \rightarrow \infty} \sum_{\mathbf{k}} f(\mathbf{k}) = \int f(\mathbf{k}) dN = \frac{V}{(2\pi)^3} \int f(\mathbf{k}) d^3k, \quad (1.83)$$

where $f(\mathbf{k})$ is an arbitrary function of $\mathbf{k}$. This rule is very important for statistical physics. Note also that if the same wave vector $\mathbf{k}$ corresponds to several internal quantum states (such as spin – see Chapter 4), the right-hand part of Eq. (83) requires multiplication by the corresponding *degeneracy factor*.

1.6. Dimensionality reduction

To conclude this introductory chapter, let me discuss the conditions when the spatial dimensionality of a wave mechanics problem may be reduced.⁵⁰ For example, following our discussion

⁴⁹ For a more detailed discussion of this point, the reader may be referred, e.g., to CM Secs. 5.4 (in the context of 1D mechanical waves), because it is valid for waves of any nature.

of the 3D rectangular, flat-bottom quantum well in Sec. 5, let us consider an infinitely deep quantum well whose bottom is flat only in one direction, say z :

$$U(\mathbf{r}) = \begin{cases} U(x, y), & \text{for } 0 < z < a_z, \\ +\infty, & \text{otherwise.} \end{cases} \quad (1.84)$$

In this case, we can separate variables only partly, by presenting the eigenfunction as $\psi(x, y)Z(z)$. Plugging such solution into the corresponding form of the stationary Schrödinger equation (63), we see that functions $Z(z)$ are again similar to those given by Eq. (76), while function $\psi(x, y)$ satisfies the following 2D stationary Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla_{x,y}^2 \psi + U_{\text{ef}}(x, y) \psi = E_{x,y} \psi, \quad (1.85)$$

2D stationary Schrödinger equation

where

$$U_{\text{ef}}(x, y) \equiv U(x, y) + E_z = U(x, y) + \frac{\pi^2 \hbar^2 n_z^2}{2ma_z^2}. \quad (1.86)$$

Effective potential energy

Thus, we have arrived at the boundary problem similar to the initial one, but with the spatial dimensionality reduced from 3 to 2, due to what is called the *partial confinement*⁵¹ in direction z . If all partial functions $Z(z)$ are normalized to unity, the wavefunction normalization condition (22c) becomes

$$W = \int_A \psi(x, y) \psi^*(x, y) dx dy, \quad (1.87)$$

where A is the total area of the system on the $[x, y]$ plane, and is formally similar to the initial 3D normalization condition. However, the effective 2D potential energy $U_{\text{ef}}(x, y)$ includes term E_z depending on quantum number n_z ,⁵² making the physical relevance of such variable separation much less general than might be naively expected. There are three possible cases:

(i) If there is no strong relation between the energy scale $E_{x,y}$ of potential $U_{\text{ef}}(x, y)$ and E_z , the solution of a typical problem has to be presented as a (typically, large) sum of partial solutions $\psi(x, y)Z(z)$, each with its own n_z , U_{ef} , and E_z . In this general case, the variable separation may not provide much relief at all, because eigenenergies of solutions with different n_z may be close, so that several of them would simultaneously participate in realistic processes.

(ii) E_z is *much smaller* than $E_{x,y}$ and may be neglected. This may be the case, for example, if the potential profile is more steep along axes x and y , than along direction z . Notice, however, that condition, $a_z \rightarrow \infty$, does not guarantee the smallness of E_z , because it may be compensated by large values of n_z . In this case (typical for solid state problems), either summation or integration over n_z still

⁵⁰ Many textbooks on quantum mechanics jump to solution of 1D without such discussion, and most of my beginning graduate students did not understand that in realistic physical systems, such dimensionality restriction is only possible under very specific conditions.

⁵¹ The term “quantum confinement”, sometimes used to describe this phenomenon, is as unfortunate as the “quantum well”, because of the same reason: the confinement is a purely classical effect, and as we will repeatedly see in this course, quantum mechanics reduces it, allowing a partial penetration of the particle into the classically forbidden regions with $E > U(\mathbf{r})$.

⁵² The last term in Eq. (86) is frequently referred to as the (partial) *confinement energy*; despite its inclusion to U_{ef} , it is important to remember about the kinetic-energy origin of this contribution.

may be needed, though sometimes may be carried out analytically, because functions $Z(z)$ are simple sinusoidal waves.

(iii) Counter-intuitively, the most robust dimensionality reduction is possible in the opposite limit, when a_z is much smaller than the characteristic scale of motion within the $[x, y]$ plane (Fig. 8a). Indeed, in this case the distance between adjacent levels of the confinement energy E_z is *much larger* than the characteristic energy $E_{x,y}$ of motion within the plane. As a result, if the system was initially prepared to be on the lowest, ground level of E_z , a “soft” motion along x and y cannot excite the system to higher levels of E_z .⁵³ Hence, the system keeps the fixed quantum number $n_z = 1$, through the motion, so that the confinement energy E_z is constant and, according to Eq. (86), may be treated just as a fixed potential energy offset.

The last conclusion is true even if the quantum well’s profile in direction z is not rectangular (provided that E_z is still much larger than $E_{x,y}$). For example, many 2D quantum phenomena, such as the quantum Hall effect,⁵⁴ have been studied experimentally using electrons confined at semiconductor heterojunctions (e.g., epitaxial interfaces GaAs/Al_xGa_{1-x}As) where the potential well in the direction perpendicular to the interface has a nearly triangular shape, with the splitting of energies E_z is the order of 10^{-2} eV.⁵⁵ This splitting energy corresponds to $k_B T$ at temperature ~ 100 K, so that careful experimentation at liquid helium temperatures (4K and below) may keep the electrons performing purely 2D motion in the “lowest subband” ($n_z = 1$).

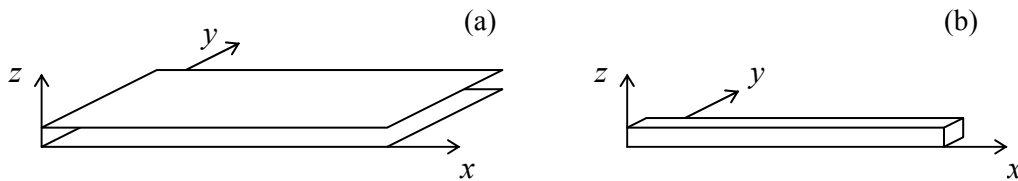


Fig. 1.8. Partial confinement in: (a) one dimension, and (b) two dimensions.

Now, if a quantum well is formed in two dimensions (say, y and z , see Fig. 8b),⁵⁶

$$U(\mathbf{r}) = \begin{cases} U(x), & \text{for } 0 < y < a_y \text{ and } 0 < z < a_z, \\ +\infty, & \text{otherwise.} \end{cases} \quad (1.88)$$

then repeating the variable separation procedure we see that the 3D Schrödinger equation (68) may be satisfied with particular solutions of the type (71), again with sinusoidal standing waves $Y(y)$ and $Z(z)$, but generally a more complex function $X(x)$, which has to satisfy the following *1D Schrödinger equation*

1D stationary
Schrödinger
equation

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} + U_{\text{ef}}(x)X = E_x X, \quad (1.89)$$

⁵³ In the frequent case when motion in the $[x, y]$ plane is free (or almost free), the set of quantum states with the same quantum number n_z is frequently called a *subband*, because their energies form a (quasi-) continuum of eigenenergies $E_{x,y}$.

⁵⁴ To be discussed in Sec. 3.2.

⁵⁵ See, e.g., P. Harrison, *Quantum Wells, Wires, and Dots*, 3rd ed., Wiley, 2010.

⁵⁶ This is a reasonable first approximation, for example, for electron motion potential in so-called *quantum wires*, for example in the now-famous carbon nanotubes – see, e.g., the same monograph by P. Harrison.

with the effective potential energy

$$U_{\text{ef}}(x) = U(x) + E_y + E_z. \quad (1.90)$$

Effective
potential
energy

Again, if the particle stays in the lowest subband, $n_y = n_z = 1$, both E_y and E_z retain their constant values E_{y1} and E_{z1} . Repeating the above discussion of the one-dimensional partial confinement, we can expect that a wave mechanics problem may be substantially simplified if E_{y1} and E_{z1} are much larger than the energy scale E_x of the motion in direction x . Namely, if:

(i) the potential profile within the 2D partial confinement plane $[y, z]$ is arbitrary (provided that it provides partial confinement scales a_y and a_z much smaller the spatial scale of the motion in direction x), and

(ii) the potential energy U is either constant in time or changes relatively slowly, at a time scale $\tau \gg \hbar/E_{yz1}$ (where E_{yz1} is the lowest eigenenergy of motion within the $[y, z]$ plane),

then a large range of experiments may be adequately described by looking for solution of the general (time-dependent, 3D) Schrödinger equation in the form of the following product

$$\Psi(x, t) YZ_1(y, z) \exp\left\{-i \frac{E_{yz1}}{\hbar} t\right\}, \quad (1.91)$$

where YZ_1 is the lowest (ground-state) eigenfunction of the 2D problem in the $[y, z]$ plane. Substituting this solution to the equation, and separating variables $\{y, z\}$ from $\{x, t\}$, we obtain the following time-dependent, 1D equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x, t) \Psi(x, t). \quad (1.92)$$

1D time-
dependent
Schrödinger
equation

The next chapter will be devoted to a detailed discussion of the wave mechanics described by this 1D equation, because it allows to study most basic phenomena and concepts of wave mechanics without involving overly complex math. In that chapter, for the notation simplicity, energy E_x 1D motion will be referred to just as E . However, one should always remember that each “1D problem” has two hidden degrees of freedom and that the genuine energy of the particle also includes a constant shift E_{yz1} which is typically much larger than E_x . The Universe is (at least :-)) 3-dimensional, and it shows!

Finally, note that in systems with reduced dimensionality, Eq. (82) for the number of states at large $\mathbf{k}$ (i.e., for an essentially free particle motion) should be replaced accordingly: in a 2D system of area $A \gg 1/k^2$,

$$dN = \frac{A}{(2\pi)^2} d^2 k, \quad (1.93)$$

2D number
of states

while in a 1D system of length $l \gg 1/k$,

$$dN = \frac{l}{2\pi} dk, \quad (1.94)$$

1D number
of states

with the corresponding changes of the summation rule (83). This change has important implications for the density of states on the energy scale, dN/dE : it is straightforward (and hence left for the reader :-)) to use Eqs. (82), (93), and (94) to show that for free 3D particles the density increases with E

(proportionally to $E^{1/2}$), for free 2D particles it does not depend on energy, while for free 1D particles it scales as $E^{-1/2}$, i.e. decreases with energy.

1.7. Exercise problems

1.1. The actual postulate made by N. Bohr in his original 1913 paper was not directly Eq. (10), but an assumption that at quantum leaps between adjacent large (quasiclassical) orbits with $n \gg 1$, hydrogen atom either emits or absorbs energy $\Delta E = \hbar\omega$, where ω is its classical radiation frequency - according to classical electrodynamics, equal to the angular velocity of electron's rotation. Prove that this postulate is indeed compatible with Eqs. (8)-(10).

1.2. Use Eq. (53) to prove that linear operators of quantum mechanics are commutative: $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$, and associative: $(\hat{A}_1 + \hat{A}_2) + \hat{A}_3 = \hat{A}_1 + (\hat{A}_2 + \hat{A}_3)$.

1.3. Prove that for any Hamiltonian operator $\hat{H}$ and two arbitrary complex functions $f(\mathbf{r})$ and $g(\mathbf{r})$,

$$\int f(\mathbf{r})\hat{H}g(\mathbf{r})d^3r = \int \hat{H}f(\mathbf{r})g(\mathbf{r})d^3r.$$

1.4. Prove that the Schrödinger equation (1.25) with Hamiltonian (1.41) is Galilean-invariant, provided that the wave function is transformed as

$$\Psi'(\mathbf{r}', t') = \Psi(\mathbf{r}, t) \exp\left\{-i\frac{m\mathbf{v} \cdot \mathbf{r}}{\hbar} + i\frac{mv^2 t}{2\hbar}\right\},$$

where the prime sign denotes the variables measured in the reference frame O' that moves, without rotation, with a constant velocity $\mathbf{v}$ relatively to the “lab” frame O . Give a physical interpretation of this transformation.

1.5.* Prove the so-called *Hellmann-Feynman theorem*:⁵⁷

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_n,$$

where λ is some parameter, on whom the Hamiltonian $\hat{H}$, and hence its eigenenergies E_n depend.

1.6. Calculate $\langle x \rangle$, $\langle p_x \rangle$, δx , and δp_x for eigenstate $\{n_x, n_y, n_z\}$ of a rectangular, infinitely deep quantum well (69). Compare product $\delta x \delta p_x$ with Heisenberg's uncertainty relation.

⁵⁷ Despite the theorem's name, H. Hellmann (in 1937) and R. Feynman (in 1939) were not the first in the long list of physicists who have (apparently, independently) discovered this fact. Indeed, it may be traced back at least to a 1922 paper by W. Pauli, and was carefully proved by P. Güttinger in 1931.

1.7. A particle, placed in a hard-wall, rectangular box with sides a_x , a_y , and a_z , is in its ground state. Calculate the average force acting on each face of the box. Can the forces be characterized by a certain pressure?

1.8. A 1D quantum particle was initially in the ground state of a very deep, rectangular quantum well of width a :

$$U(x) = \begin{cases} 0, & \text{for } -a/2 < x < +a/2, \\ +\infty, & \text{otherwise.} \end{cases}$$

At some instant, the well's width is abruptly increased to value $a' > a$ (leaving the well symmetric about point $x = 0$), and then left constant. Calculate the probability that after the change, the particle is still in the ground state of the system.

1.9. At $t = 0$, a 1D particle of mass m is placed into a hard-wall, flat-bottom potential well

$$U(x) = \begin{cases} 0, & \text{for } 0 < x < a, \\ +\infty, & \text{otherwise,} \end{cases}$$

in a 50/50 linear superposition of the lowest (ground) and the first excited states, so that its wavefunction at that instant is

$$\Psi(x, 0) = C [\psi_g(x) + \psi_e(x)],$$

where C is the normalization constant which ensures that the particle is (somewhere) in the well with probability $W = 1$. Calculate:

- (i) the normalized wavefunction $\Psi(x, t)$ for arbitrary time t , and
- (ii) the time evolution of the expectation value $\langle x \rangle$ of particle's coordinate.

1.10. Find the potential profile $U(x)$ for which the following wavefunctions,

- (i) $\Psi = c \exp\{-ax^2 - ibt\}$, and
- (ii) $\Psi = c \exp\{-a|x| - ibt\}$,

(with real coefficients $a > 0$ and b), satisfy the Schrödinger equation for a particle with mass m . For each case, calculate $\langle x \rangle$, $\langle p_x \rangle$, δx , and δp_x , and compare the product $\delta x \delta p_x$ with Heisenberg's uncertainty relation.

1.11. Calculate the energy density dN/dE of traveling wave states in large rectangular quantum wells of various dimensions: $d = 1, 2$, and 3 .

1.12.* Use the finite difference method with steps $a/2$ and $a/3$ to find as many eigenenergies as possible for a particle in the infinitely deep, hard-wall quantum well of width a . Compare the results with each other, with the exact formula.⁵⁸

⁵⁸ You may like to start from reading about the finite-difference method - see, e.g., CM Sec. 8.5 or EM Sec. 2.8.

Chapter 2. 1D Wave Mechanics

The main goal of this chapter is the solution and discussion of a few conceptually most important problems of wave mechanics for the simplest, 1D case. This lowest dimensionality, and a wide use of potential profiles' approximation by sets of Dirac's delta-functions, simplify the necessary calculations considerably without sacrificing the physical essence of the described phenomena. The reader is advised to pay special attention to Sections 6-9, which cover some important material not usually discussed in textbooks.

2.1. Probability current and uncertainty relations

As was discussed in the end of Chapter 1, in several cases (most importantly, at strong confinement within the $[y, z]$ plane), the general (3D) Schrödinger equation may be reduced to the 1D equation (1.92):

Schrödinger
equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x, t) \Psi(x, t). \quad (2.1)$$

If the transversal factor – say, the function $YZ_1(y, z)$ that participates in Eq. (1.91), is normalized to unity, then the integration of Eq. (1.22a) over a segment $[x_1, x_2]$, gives the probability to find the particle on this segment:

Probability

$$W(t) \equiv \int_{x_1}^{x_2} \Psi(x, t) \Psi^*(x, t) dx. \quad (2.2)$$

If the particle under analysis is definitely inside the system, the normalization of its 1D wavefunction $\Psi(x, t)$ is provided by extending integral (2) to the whole axis x :

Normalization

$$\int_{-\infty}^{+\infty} w(x, t) dx = 1, \quad \text{where } w(x, t) \equiv \Psi(x, t) \Psi^*(x, t). \quad (2.3)$$

A similar integration of Eq. (1.23) shows that the expectation value of any operator depending only on coordinate x (and possibly time), may be expressed as

Expectation
value

$$\langle A \rangle(t) = \int_{-\infty}^{+\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx. \quad (2.4)$$

It is also useful to introduce the probability current along the x -axis (a *scalar*):

Probability
current

$$I(x, t) \equiv \int j_x dy dz = \frac{\hbar}{m} \operatorname{Im} \left(\Psi^* \frac{\partial}{\partial x} \Psi \right) = \frac{\hbar}{m} |\Psi(x, t)|^2 \frac{\partial \varphi}{\partial x}, \quad (2.5)$$

where j_x is x -component of the probability current density *vector* $\mathbf{j}(\mathbf{r}, t)$. Then the continuity equation (1.48) for the segment $[x_1, x_2]$ takes the form

Continuity
equation

$$\frac{dW}{dt} + I(x_2) - I(x_1) = 0. \quad (2.6)$$

The above formulas are the basis for the analysis of 1D problems of wave mechanics, but before proceeding to particular cases, let me deliver on my earlier promise to prove that Heisenberg's uncertainty relation (1.35) is indeed valid for any wavefunction $\Psi(x,t)$. For that, let us consider an evidently positive (or at least non-negative) integral

$$J(\lambda) \equiv \int_{-\infty}^{+\infty} \left| x\Psi + \lambda \frac{\partial \Psi}{\partial x} \right|^2 dx \geq 0, \quad (2.7)$$

where λ is an arbitrary real constant, and assume that at the at $x \rightarrow \pm\infty$ the wavefunction vanishes, together with its first derivative. The left-hand part of Eq. (7) may be recast as

$$\begin{aligned} \int_{-\infty}^{+\infty} \left| x\Psi + \lambda \frac{\partial \Psi}{\partial x} \right|^2 dx &= \int_{-\infty}^{+\infty} \left(x\Psi + \lambda \frac{\partial \Psi}{\partial x} \right) \left(x\Psi + \lambda \frac{\partial \Psi}{\partial x} \right)^* dx \\ &= \int_{-\infty}^{+\infty} x^2 \Psi \Psi^* dx + \lambda \int_{-\infty}^{+\infty} x \left(\Psi \frac{\partial \Psi^*}{\partial x} + \frac{\partial \Psi}{\partial x} \Psi^* \right) dx + \lambda^2 \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} dx. \end{aligned} \quad (2.8)$$

According to Eq. (4), the first term in the last form of Eq. (8) is just $\langle x^2 \rangle$. The second and the third integrals may be worked out by parts:

$$\int_{-\infty}^{+\infty} x \left(\Psi \frac{\partial \Psi^*}{\partial x} + \frac{\partial \Psi}{\partial x} \Psi^* \right) dx = \int_{-\infty}^{+\infty} x \frac{\partial}{\partial x} (\Psi \Psi^*) dx = \int_{-\infty}^{+\infty} x d(\Psi \Psi^*) = \Psi \Psi^* x \Big|_{x=-\infty}^{x=+\infty} - \int_{-\infty}^{+\infty} \Psi \Psi^* dx = -1, \quad (2.9)$$

$$\int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} dx = \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} d\Psi^* = \frac{\partial \Psi}{\partial x} \Psi^* \Big|_{x=-\infty}^{x=+\infty} - \int_{-\infty}^{+\infty} \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \Psi^* \hat{p}_x^2 \Psi dx = \frac{\langle p_x^2 \rangle}{\hbar^2}. \quad (2.10)$$

As a result, Eq. (7) takes the following form:

$$J(\lambda) = \langle x^2 \rangle - \lambda + \lambda^2 \frac{\langle p_x^2 \rangle}{\hbar^2} \geq 0, \quad \text{i.e. } \lambda^2 + a\lambda + b \geq 0, \quad \text{with } a \equiv -\frac{\hbar^2}{\langle p_x^2 \rangle} \text{ and } b \equiv \frac{\hbar^2 \langle x^2 \rangle}{\langle p_x^2 \rangle}. \quad (2.11)$$

This inequality should be valid for any real λ , i.e. the corresponding quadratic equation, $\lambda^2 + a\lambda + b = 0$, can have either one (degenerate) real root - or no real roots at all. This is only possible if its determinant, $\text{Det} = a^2 - 4b$, is non-positive, leading to the following requirement:

$$\langle x^2 \rangle \langle p_x^2 \rangle \geq \frac{\hbar^2}{4}. \quad (2.12)$$

In particular, if $\langle x \rangle = 0$ and $\langle p_x \rangle = 0$,¹ then according to Eq. (1.33), Eq. (12) takes the form

$$\boxed{\langle \tilde{x}^2 \rangle \langle \tilde{p}_x^2 \rangle \geq \frac{\hbar^2}{4}}, \quad (2.13)$$

Heisenberg's
uncertainty
relation

which, according to the definition (1.34) of r.m.s. uncertainties, is equivalent to Eq. (1.35).

¹ Eq. (13) may be proved even if $\langle x \rangle$ and $\langle p_x \rangle$ are not equal to zero, by making the following replacements, $x \rightarrow x - \langle x \rangle$, $\partial/\partial x \rightarrow \partial/\partial x + i\langle p \rangle/\hbar$, in Eq. (7), and then repeating all the calculations – which become rather bulky. We will re-derive the uncertainty relations, in a more efficient way, in Chapter 4.

Now let us notice that the Heisenberg's uncertainty relation looks very similar to the *commutation relation* between the corresponding operators:

$$[\hat{x}, \hat{p}_x]\Psi \equiv (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\Psi = -i\hbar x \frac{\partial\Psi}{\partial x} + i\hbar \frac{\partial}{\partial x}(x\Psi) = i\hbar\Psi. \quad (2.14a)$$

Since this relation is valid for arbitrary wavefunction $\Psi(x, t)$, we may present it as an operator equality:

$$[\hat{x}, \hat{p}_x] = i\hbar \neq 0. \quad (2.14b)$$

Coordinate/
momentum
operators'
commutator

In Sec. 4.5 we will see that the relation between Eqs. (13) and (14) is just a particular case of a general relation between the expectation values of non-commuting operators and their commutators.

2.2. Free particle: Wave packets

Let us start our discussion of particular problems with free the 1D motion, with $U(x, t) = 0$. From our discussion of Eq. (1.29) in Chapter 1, it is clear that in the 1D case, a similar “fundamental” (i.e. a particular but the most important) solution of the Schrödinger equation (1) is a monochromatic wave

$$\Psi_0(x, t) = \text{const} \times e^{i(k_0 x - \omega_0 t)}. \quad (2.15)$$

According to Eqs. (1.32), it corresponds to a particle with an exactly defined momentum² $p_0 = \hbar k_0$ and energy $E_0 = \hbar\omega_0 = \hbar^2 k_0^2 / 2m$. However, for this wavefunction, product $\Psi^*\Psi$ does not depend on either x or t , so that the particle is completely delocalized, i.e. its probability is spread all over axis x , at all times. (As a result, such state is still compatible with Heisenberg's uncertainty relation (13), despite the exact value p_0 of momentum p .)

In order to describe a space-localized particle, let us form, at the initial moment of time ($t = 0$), a wave packet of the type shown in Fig. 1.6, by multiplying the sinusoidal waveform (15) by some smooth *envelope function* $A(x)$. As the most important particular example, consider a *Gaussian packet*

$$\Psi(x, 0) = A(x)e^{ik_0 x}, \quad \text{with } A(x) = \frac{1}{(2\pi)^{1/4}(\delta x)^{1/2}} \exp\left\{-\frac{x^2}{2(\delta x)^2}\right\}. \quad (2.16)$$

Initial
Gaussian
wave
packet

(By the way, Fig. 1.6 shows exactly such a packet.) The pre-exponential factor in this envelope function has been selected in the way to have the initial probability density,

$$w(x, 0) = \Psi^*(x, 0)\Psi(x, 0) = A^*(x)A(x) = \frac{1}{(2\pi)^{1/2} \delta x} \exp\left\{-\frac{x^2}{2(\delta x)^2}\right\}, \quad (2.17)$$

normalized according to Eq. (3), for any parameters δx and k_0 .³

In order to explore the evolution of this packet in time, we could try to solve Eq. (1) with the initial condition (16) directly, but in the spirit of the discussion in Sec. 1.5, it is easier to proceed

² From this point on, in this chapter I will drop index x in notation for x -component of vectors $\mathbf{k}$ and $\mathbf{p}$.

³ This may be readily proven using the well-known integral of the Gaussian function (“bell curve”) given by Eq. (17) – see, e.g., MA Eq. (6.9b). It is also straightforward to use MA Eq. (6.9c) to prove that for wave packet (16), parameter δx is indeed the r.m.s. uncertainty (1.34) of coordinate x , thus justifying its notation.

differently. Let us first present the initial wavefunction (16) as a sum (1.65) of eigenfunctions $\psi_k(x)$ of the corresponding stationary 1D Schrödinger equation (1.60), in our current case

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_k}{dx^2} = E_k \psi_k, \quad \text{with } E_k \equiv \frac{\hbar^2 k^2}{2m}, \quad (2.18)$$

that are simply monochromatic waves,

$$\psi_k = a_k e^{ikx}, \quad (2.19)$$

with a continuum spectrum of possible wave numbers k . For that, sum (1.65) should be replaced with an integral:⁴

$$\Psi(x,0) = \int a_k \psi_k(x) dp = \int a_k e^{ikx} dk. \quad (2.20)$$

Now let us notice that from the point of view of mathematics, Eq. (20) is just the usual Fourier transform from variable k to the “conjugate” variable x , and we can use the well-known formula of the reciprocal Fourier transform to calculate

$$a_k = \frac{1}{2\pi} \int \Psi(x,0) e^{-ikx} dx = \frac{1}{2\pi} \frac{1}{(2\pi)^{1/4} (\delta x)^{1/2}} \int \exp \left\{ -\frac{x^2}{(2\delta x)^2} - i\tilde{k}x \right\} dx, \quad \text{where } \tilde{k} \equiv k - k_0, \quad (2.21)$$

This *Gaussian integral* may be worked out by the following standard method. Let us complement the exponent to the full square of a linear combination of x and k , plus a term independent of x :

$$-\frac{x^2}{(2\delta x)^2} - i\tilde{k}x = -\frac{1}{(2\delta x)^2} \left[x + 2i\tilde{k}(\delta x)^2 \right]^2 - \tilde{k}^2 (\delta x)^2. \quad (2.22)$$

Since the integration in the right-hand part of Eq. (20) should be performed at constant $\tilde{k}$, in the infinite limits, its result would not change if we replace dx by $dx' \equiv d[x + 2i\tilde{k}(\delta x)^2 \tilde{k}]$.⁵ As a result, we get,

$$a_k = \frac{1}{2\pi} \frac{1}{(2\pi)^{1/4} (\delta x)^{1/2}} \exp \left\{ -\tilde{k}^2 (\delta x)^2 \right\} \int \exp \left\{ -\frac{x'^2}{(2\delta x)^2} \right\} dx' = \left(\frac{1}{2\pi} \right)^{1/2} \frac{1}{(2\pi)^{1/4} (\delta k)^{1/2}} \exp \left\{ -\frac{\tilde{k}^2}{(2\delta k)^2} \right\}. \quad (2.23)$$

so that a_k also has a Gaussian distribution, now along axis k , centered to value k_0 (Fig. 1.6b), with constant δk defined as

$$\delta k \equiv 1/2\delta x. \quad (2.24)$$

Thus we may present the initial wave packet (16) as

$$\Psi(x,0) = \left(\frac{1}{2\pi} \right)^{1/2} \frac{1}{(2\pi)^{1/4} (\delta k)^{1/2}} \int \exp \left\{ -\frac{(k - k_0)^2}{(2\delta k)^2} \right\} e^{ikx} dk. \quad (2.25)$$

From comparison of this formula with Eq. (16), it is evident that the r.m.s. uncertainty of the wave number k in this packet is indeed equal to δk defined by Eq. (24), thus justifying the notation. The

⁴ For notation's brevity, from this point on the infinite limit signs will be dropped in all 1D integrals.

⁵ The fact that the argument shift is imaginary is not important, because function under the integral is analytical, and tends to zero at $\text{Re } x' \rightarrow \pm\infty$.

comparison of that relation with Eq. (1.35) shows that the Gaussian packet presents the ultimate case in which the product $\delta x \delta p = \delta x (\hbar \delta k)$ has the lowest possible value ($\hbar/2$); for any other envelope's shape the uncertainty product may only be larger. We could of course get the same result for δk from Eq. (16) using definitions (1.23), (1.33), and (1.34); the real advantage of Eq. (24) is that it can be readily generalized to $t > 0$.

Indeed, we already know that the time evolution of the wavefunction is given by Eq. (1.67), for our case giving⁶

$$\Psi(x, t) = \left(\frac{1}{2\pi} \right)^{1/2} \frac{1}{(2\pi)^{1/4} (\delta k)^{1/2}} \int \exp \left\{ -\frac{(k - k_0)^2}{(2\delta k)^2} \right\} e^{ikx} \exp \left\{ -i \frac{\hbar k^2}{2m} t \right\} dk. \quad (2.26)$$

Fig. 1 shows several snapshots of the real part of wavefunction (26), for a particular case $\delta k = 0.1 k_0$.

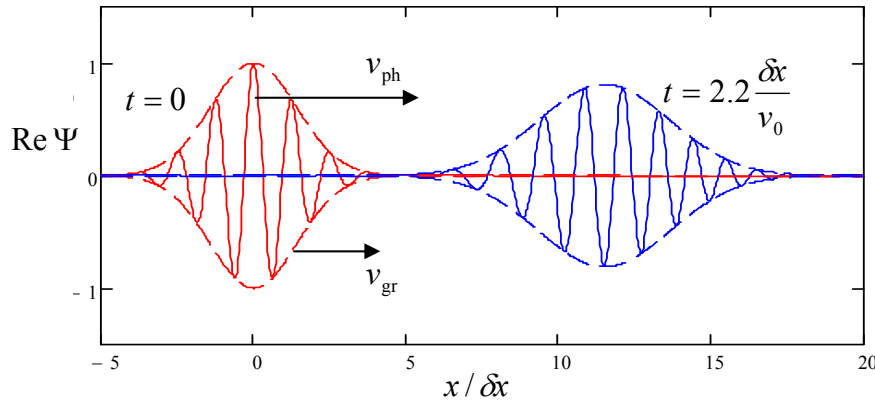
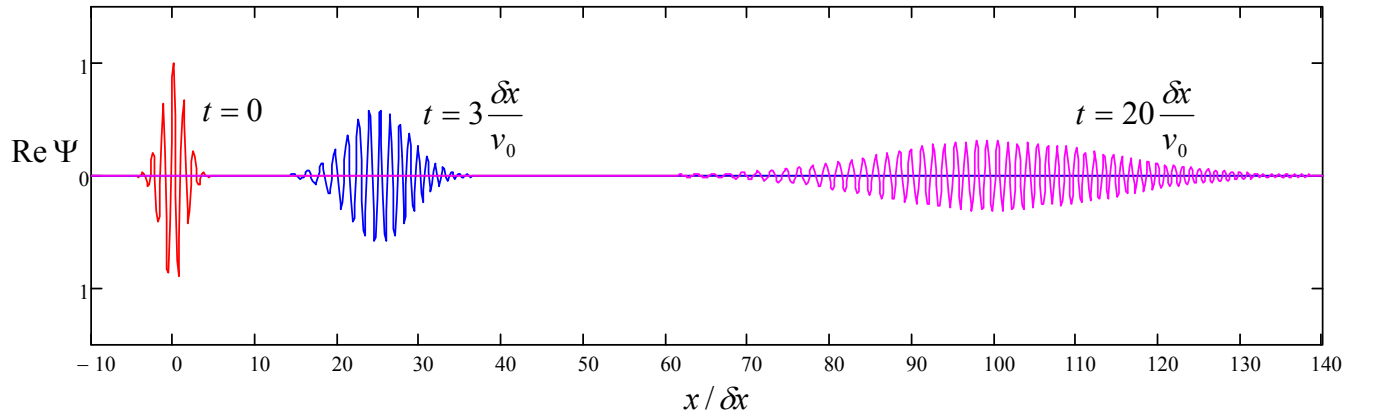


Fig. 2.1. Time evolution of the wave 1D wave packet evolution on: (a) a smaller and (b) larger time scales. Dashed lines show packet's envelope, i.e. $\pm |\Psi|$.



The plots clearly show the following effects:

(i) the wave packet as a whole (as characterized by its envelope) moves along the x axis with a certain *group velocity* v_{gr} ,

⁶ Note that this packet is equivalent to Eq. (16) and hence is properly normalized to 1 – see Eq. (3). Hence the wave packet introduction offers a natural solution to the problem of infinite wave normalization, which was mentioned in Sec. 1.2.

(ii) the “carrier” wave inside the packet moves with a different, *phase velocity* v_{ph} , which may be defined as the velocity the spatial points where wave’s phase $\varphi(x, t) \equiv \arg \Psi$ takes a certain fixed value (say, $\varphi = \pi/2$, where $\text{Re} \Psi$ vanishes), and

(iii) the packet’s spatial width gradually increases with time - the packet *spreads*.

All these effects are common for waves of any physical nature.⁷ Indeed, let us consider a 1D wave packet of the type (26),

$$\Psi(x, t) = \int a_k e^{i(kx - \omega t)} dk, \quad (2.27)$$

Arbitrary
wave
packet

propagating in a media with an arbitrary (but smooth!) dispersion relation $\omega(k)$, and assume that the wave number distribution a_k is arbitrary but narrow: $\delta k \ll \langle k \rangle \equiv k_0$ - see Fig. 1.6b. Then we may expand function $\omega(k)$ into the Taylor series near the central point k_0 , and keep only two of its leading terms:

$$\omega(k) \approx \omega_0 + \frac{d\omega}{dk} \tilde{k} + \frac{1}{2} \frac{d^2\omega}{dk^2} \tilde{k}^2, \quad \text{where } \tilde{k} \equiv k - k_0, \quad \omega_0 \equiv \omega(k_0), \quad (2.28)$$

and both derivatives are also evaluated at point $k = k_0$. In this approximation,⁸ the expression in parentheses in the right-hand part of Eq. (27) may be rewritten as

$$kx - \omega t = k_0 x + \tilde{k} x - \left(\omega_0 + \frac{d\omega}{dk} \tilde{k} + \frac{1}{2} \frac{d^2\omega}{dk^2} \tilde{k}^2 \right) t = (k_0 x - \omega_0 t) + \tilde{k} \left(x - \frac{d\omega}{dk} t \right) - \frac{1}{2} \frac{d^2\omega}{dk^2} \tilde{k}^2 t, \quad (2.29)$$

so that Eq. (27) is reduced to integral

$$\Psi(x, t) = e^{i(k_0 x - \omega_0 t)} \int a_k \exp \left\{ i \left[\tilde{k} \left(x - \frac{d\omega}{dk} t \right) - \frac{1}{2} \frac{d^2\omega}{dk^2} \tilde{k}^2 t \right] \right\} d\tilde{k}. \quad (2.30)$$

First, let neglect the last term in square brackets (which is much smaller than the first term if the dispersion relation is smooth enough and/or the time interval t is sufficiently small), and compare the result with the initial form of the wave packet (27)

$$\Psi(x, 0) = \int a_k e^{ikx} dk = A(x) e^{ik_0 x}, \quad \text{with } A(x) \equiv \int a_k e^{i\tilde{k}x} d\tilde{k}. \quad (2.31)$$

The comparison shows that Eq. (30) is reduced to

$$\Psi(x, t) = A(x - v_{gr} t) e^{ik_0(x - v_{ph} t)}, \quad (2.32)$$

where v_{gr} and v_{ph} are two constants with the dimension of velocity:

$$v_{gr} \equiv \left. \frac{d\omega}{dk} \right|_{k=k_0}, \quad \text{and} \quad v_{ph} \equiv \left. \frac{\omega}{k} \right|_{k=k_0}. \quad (2.33)$$

Group
and phase
velocities

It is clear that Eq. (32) describes effects (i) and (ii) listed above. Let us calculate the group and phase velocities for the particular case of de Broglie waves whose dispersion law is given by Eq. (1.30):

⁷ See, e.g., brief discussions in CM Sec. 5.3 and EM Sec. 7.2.

⁸ By the way, in the particular case of de Broglie wave described by dispersion relation (1.30), Eq. (28) is exact, because $\omega = E/\hbar$ is a quadratic function of $k = p/\hbar$, and all higher derivatives of ω over k vanish for any k_0 .

$$\omega = \frac{\hbar k^2}{2m}, \quad v_{\text{gr}} \equiv \left. \frac{d\omega}{dk} \right|_{k=k_0} = \frac{\hbar k_0}{m} \equiv v_0, \quad v_{\text{ph}} \equiv \left. \frac{\omega}{k} \right|_{k=k_0} = \frac{\hbar k_0}{2m} = \frac{v_{\text{gr}}}{2}. \quad (2.34)$$

We see that (very fortunately!) the velocity of the wave packet envelope is constant and equals to that of the classical particle moving by inertia, in accordance with the correspondence principle.

The remaining term in the square brackets of Eq. (30) describes effect (iii), the wave packet's spread. It may be readily evaluated if the packet (27) is initially Gaussian, as in our example (25):

$$a_k = \text{const} \times \exp \left\{ -\frac{\tilde{k}^2}{(2\delta k)^2} \right\}. \quad (2.34)$$

In this case integral (30) is Gaussian, and may be worked out exactly as integral (20), i.e. merging the exponents under the integral, and presenting them as a full square of linear combination of x and k :

$$-\frac{\tilde{k}^2}{(2\delta k)^2} + i\tilde{k}(x - v_{\text{gr}}t) - \frac{i}{2} \frac{d^2\omega}{dk^2} \tilde{k}^2 t = -\Delta(t) \left(\tilde{k} + i \frac{x - v_{\text{gr}}t}{2\Delta(t)} \right)^2 - \frac{(x - v_{\text{gr}}t)^2}{4\Delta(t)} + ik_0x - \frac{i}{2} \frac{d^2\omega}{dk^2} k_0^2 t, \quad (2.35)$$

where I have introduced the following complex function of time:

$$\Delta(t) \equiv \frac{1}{4(\delta k)^2} + \frac{i}{2} \frac{d^2\omega}{dk^2} t = (\delta x')^2 + \frac{i}{2} \frac{d^2\omega}{dk^2} t, \quad (2.36)$$

and have used Eq. (24) in the second equality. Now integrating over $\tilde{k}$, we get

$$\Psi(x, t) \propto \exp \left\{ -\frac{(x - v_{\text{gr}}t)^2}{4\Delta(t)} + i \left(k_0x - \frac{1}{2} \frac{d^2\omega}{dk^2} k_0^2 t \right) \right\}. \quad (2.37)$$

The imaginary part of ratio $1/\Delta(t)$ in the exponent gives just an additional contribution to wave's phase, and does not affect the resulting probability distribution

$$w(x, t) = \Psi^* \Psi \propto \exp \left\{ -\frac{(x - v_{\text{gr}}t)^2}{2} \text{Re} \frac{1}{\Delta(t)} \right\}. \quad (2.38)$$

This is again a Gaussian bell curve spread over axis x , centered to point $\langle x \rangle = v_{\text{gr}}t$, with the r.m.s. width

$$(\delta x')^2 \equiv \left\{ \text{Re} \left[\frac{1}{\Delta(t)} \right] \right\}^{-1} = (\delta x)^2 + \left(\frac{1}{2} \frac{d^2\omega}{dk^2} t \right)^2 \frac{1}{(\delta x)^2}. \quad (2.39a)$$

In the particular case of de Broglie waves, $d^2\omega/dk^2 = \hbar/m$, so that

$$(\delta x')^2 = (\delta x)^2 + \left(\frac{\hbar t}{2m} \right)^2 \frac{1}{(\delta x)^2}. \quad (2.39b)$$

The physics of the spreading is very simple: if $d^2\omega/dk^2 \neq 0$, the group velocity $d\omega/dk$ of each small group dk of monochromatic components of the wave packet is different, resulting in the gradual (eventually, linear) accumulation of the differences of the distances traveled by the groups. The most curious feature of Eq. (39) is that the packet width at $t > 0$ depends on its initial width $\delta x'(0) = \delta x$ in a

Wave
packet's
spread
with time

non-monotonic way, tending to infinity at both $\delta x \rightarrow 0$ and $\delta x \rightarrow \infty$. Because of that, for a fixed t , there is an optimal value of δx with minimizes $\delta x'$:

$$(\delta x')_{\min} = \sqrt{2} (\delta x)_{\text{opt}} = \left(\frac{\hbar t}{m} \right)^{1/2}. \quad (2.40)$$

This expression may be used for spreading effect estimates. Due to the smallness of the Planck constant $\hbar$ on the human scale of things, for macroscopic bodies this effect is extremely small even for very long time intervals; however, for light particles it may be very noticeable: for the electron ($m = m_e \approx 10^{-30}$ kg), and $t = 1$ s, Eq. (40) yields $(\delta x')_{\min} \sim 1$ cm!

Note also that for any $t \neq 0$, the wave packet retains its Gaussian envelope, but the ultimate relation (24) is *not* satisfied, $\delta x' \delta p > \hbar/2$ - due to a gradually accumulated phase shift between the component monochromatic waves. The last remark on this topic: in quantum mechanics, the wave packet spreading is *not* an ubiquitous effect! For example, in Chapter 5 we will see that in a quantum oscillator, the spatial width of a Gaussian packet (for that system, called the *Glauber state*) does not grow monotonically but rather either stays constant or oscillates in time.

Now let us briefly discuss the case when the initial wave packet is not Gaussian, but is described by an arbitrary initial wavefunction. In order to make the forthcoming result more appealing, it is beneficial to generalize our calculations to an arbitrary initial time t_0 ; it is evident that if U does not depend on time explicitly, it is sufficient to replace t with $(t - t_0)$ in all above formulas. With this replacement, Eq. (27) becomes

$$\Psi(x, t) = \int a_k e^{i[kx - \omega(t - t_0)]} dk, \quad (2.41)$$

and the reciprocal transform (21) reads

$$a_k = \frac{1}{2\pi} \int \Psi(x, t_0) e^{-ikx} dx. \quad (2.42)$$

If we want to express these two formulas with one relation, i.e. plug Eq. (42) into Eq. (41), we should give the integration variable x some other name, e.g., x_0 . The result is

$$\Psi(x, t) = \frac{1}{2\pi} \int dk \int dx_0 \Psi(x_0, t_0) e^{i[k(x - x_0) - \omega(t - t_0)]}. \quad (2.43)$$

Changing the order of integration, this expression may be rewritten in the following general form:

$$\Psi(x, t) = \int G(x, t; x_0, t_0) \Psi(x_0, t_0) dx_0, \quad (2.44)$$

1D
propagator:
definition

where function G , usually called *kernel* in mathematics, in quantum mechanics is called the *propagator*.⁹ According to Eq. (43), in our particular case of a free particle the propagator is equal to

⁹ Its standard notation by letter G stems from the fact that the propagator is essentially the spatial-temporal *Green's function* of Eq. (2.18), defined very similarly to Green's functions of other ordinary and partial differential equations describing various physics systems – see, e.g., CM Sec. 4.1 and/or EM Sec. 2.7 and 7.3.

$$G(x, t; x_0, t_0) = \frac{1}{2\pi} \int e^{i[k(x-x_0) - \omega(t-t_0)]} dk, \quad (2.45)$$

The physical sense of the propagator may be understood by considering the following special initial conditions:¹⁰

$$\Psi(x_0, t_0) = \delta(x_0 - x'), \quad (2.46)$$

where x' is a certain point within the domain of particle's motion. In this particular case, Eq. (44) evidently gives

$$\Psi(x, t) = G(x, t; x', t_0). \quad (2.47)$$

Hence, the propagator, considered as a function of x and t only, is just the solution of the linear differential equation with δ -functional initial conditions. Thus while Eq. (41) may be understood as a mathematical expression of the linear superposition principle in the momentum (i.e., reciprocal) space domain, Eq. (44) is an expression of this principle in the direct space domain: the system's "response" $\Psi(x, t)$ to an arbitrary initial condition $\Psi(x_0, t_0)$ is just a sum of its responses to its thin spatial "slices", with propagator $G(x, t; x_0, t_0)$ representing the weight of each slice in the final sum.

Calculating integral (45), one should remember that ω is not a constant but a function of k , given by the dispersion relation for particular waves. In particular, for the de Broglie waves

$$G(x, t; x_0, t_0) \equiv \frac{1}{2\pi} \int \exp \left\{ i \left[k(x - x_0) - \frac{\hbar k^2}{2m} (t - t_0) \right] \right\} dk. \quad (2.48)$$

This is a Gaussian integral again, and may be readily calculated just it was done (twice) above, by completing the exponent to the full square. The result is

$$G(x, t; x_0, t_0) = \left(\frac{m}{2\pi i \hbar (t - t_0)} \right)^{1/2} \exp \left\{ -\frac{m(x - x_0)^2}{2i \hbar (t - t_0)} \right\}. \quad (2.49)$$

Please note the following features of this complex function (plotted in Fig. 2):

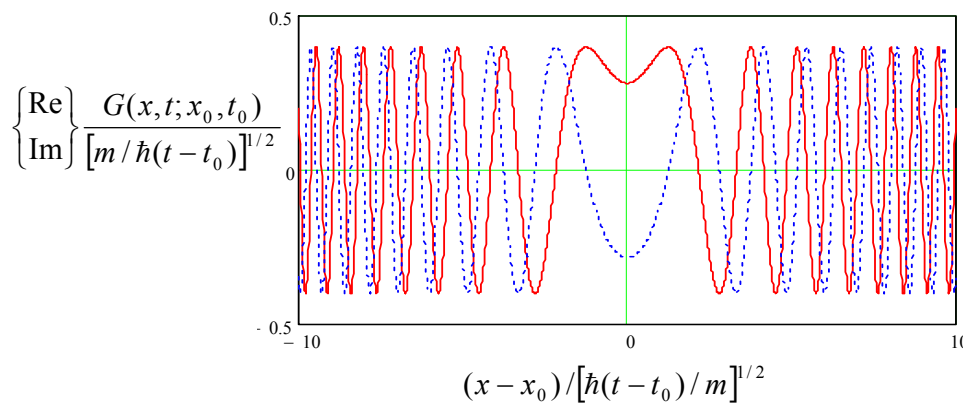


Fig. 2.2. Real (solid line) and imaginary (dashed line) parts of the 1D free particle's propagator.

¹⁰ Note that this initial condition is *not* equivalent to a δ -functional initial probability density (2).

(i) It depends only on differences $(x - x_0)$ and $(t - t_0)$. This is natural, because the free-particle propagation problem is uniform (*translation-invariant*) both in space and time.

(ii) The function shape does not depend on its arguments – they just rescale the same function: its snapshot (Fig. 2), if plotted as a function of un-normalized x , just becomes broader and lower with time. It is curious that the spatial broadening scales as $(t - t_0)^{1/2}$ – just as at the classical diffusion, as a result of a deep analogy between quantum mechanics and classical statistics – to be discussed further in Chapter 7.

(iii) In accordance with the uncertainty relation, the ultimately compressed wave packet (46) has an infinite width of momentum distribution, and the quasi-sinusoidal tails of the free-particle propagator, clearly visible in Fig. 2, are the results of the free propagation of the fastest (highest-momentum) components of that distribution, in both directions from the packet center. In the following sections, we will mostly focus on the spatial distribution of stationary, monochromatic wavefunctions (that, for unconfined motion, may be interpreted as wave packets of very large spatial width δx), only rarely coming back to the wave packet discussion. Our excuse is the linear superposition principle, i.e. our conceptual ability to restore the general solution from that of monochromatic waves of all possible energies. However, the reader should not forget that, as the above discussion has illustrated, mathematically this restoration is not always trivial.

2.3. Particle motion in simple potential profiles

Now, let us proceed to the cases in which the potential energy $U(x, t)$ is not identically equal to zero. The easiest case is that of spatially-uniform but time-dependent potential: $U = U(t) = \text{const}$. Indeed, the corresponding Schrödinger equation (1.25) with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(t) = -\frac{\hbar^2}{2m} \nabla^2 + U(t), \quad (2.50)$$

allows the variable separation similar to that performed in Sec. 1.5, besides that the time-dependent function $T(t)$ obeys an equation of motion that is slightly more general than Eq. (1.59):

$$i\hbar \dot{T} = [E - U(t)]T, \quad (2.51)$$

whose solution may be expressed as an evident generalization of Eq. (1.61):

$$T(t) = T(0)e^{-i[\omega t + \varphi(t)]}, \quad \text{with } \omega = \frac{E}{\hbar} \text{ and } \frac{d\varphi}{dt} = -\frac{U(t)}{\hbar}. \quad (2.52)$$

Looking at the basic relations (1.22) and (1.23) of wave mechanics, it seems that this additional phase factor does not affect the particle probability distribution, or even any observable (including energy it is referred to the instant value of U), and hence the phase increment φ , associated with $U(t)$, is just a mathematical artifact. This is certainly true for a single particle, however, the situation changes as soon as we recall that the Universe consists of more than one of them.

For example, consider two similar, independent particles, each in the same (say, ground) eigenstate, but with the potential energies (and hence eigenenergies $E_{1,2}$) different by a constant $\Delta U \equiv U_1 - U_2$. Then, the difference $\varphi \equiv \varphi_1 - \varphi_2$ of their wavefunction phases evolves in time as

$$\frac{d\varphi}{dt} = -\frac{\Delta U}{\hbar}. \quad (2.53)$$

If the particles are in different worlds (or at least in different laboratories :-), this evolution is unobservable; however, it should be intuitively clear that a very weak coupling of a certain detector to each particle may allow it to observe phase φ , while keeping the particle dynamics virtually unperturbed, i.e. Eq. (53) intact.

Perhaps the most dramatic demonstration of this phenomenon is the *Josephson effect* in superconductors.¹¹ Experimentally, the easiest way to observe the effect is by connecting two bulk superconductor samples with a weak, short electric contact (called either the *weak link* or the *Josephson junction*) and bias them with a constant (dc) voltage V , typically in a few-microvolt range – see Fig. 3.

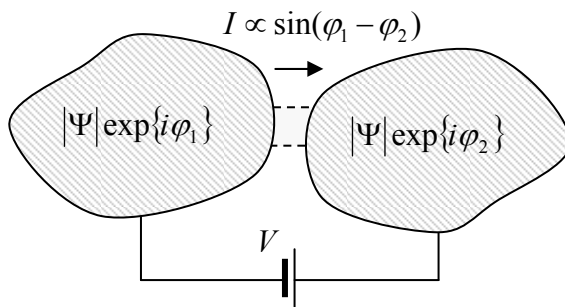


Fig. 2.3. Josephson effect in a weak link between two bulk superconductor electrodes.

Superconductivity may be explained by a specific coupling between its conduction electrons, that leads, at low temperatures, to formation of the so-called *Cooper pairs*. Such pairs, each consisting of two electrons with opposite spins and momenta, behave as Bose particles, and form coherent *Bose-Einstein condensate*.¹² Most properties of such a condensate may be described by a single wavefunction, evolving in time as that of a free particle with the effective potential energy $U = q\phi = -2e\phi$, where ϕ is the electrochemical potential,¹³ and $q = -2e$ is the total charge of the Cooper pair. As a result, for the situation shown in Fig. 3, Eq. (53) takes the form

$$\frac{d\varphi}{dt} = \frac{2e}{\hbar}V, \quad (2.54)$$

where $V = \phi_1 - \phi_2$ is the applied voltage. B. Josephson has predicted that, in a particular case when a weak link is a *tunnel junction*, electric current I of Cooper pairs through it should have a simple form:¹⁴

$$I = I_c \sin \varphi, \quad (2.55)$$

¹¹ It was predicted theoretically by B. Josephson (then a graduate student!) in 1962 and observed experimentally in less than a year. More recently, analogs of this effect were also observed in superfluid helium and atomic Bose-Einstein condensates.

¹² See, e.g., SM Sec. 3.4.

¹³ For more on this notion see, e.g. SM Sec. 6.4.

¹⁴ Later, Eq. (55) has been shown to be valid for other weak link types as well, though deviations from have also been found. These deviations, however, do not affect the fundamental 2π -periodicity of function $I(\varphi)$ – see, e.g., EM Sec. 6.4. As a result, no deviations from the fundamental relations (56)-(57) have been found (yet :-).

where I_c is some constant (scaling as the weak link strength). Combining Eqs. (53) and (54), we see that if the applied voltage is constant in time, the current oscillates with the so-called *Josephson frequency*

$$f_J = \frac{\omega_J}{2\pi}, \quad \text{where } \omega_J \equiv \frac{2e}{\hbar} \bar{V}, \quad (2.56)$$

as high as ~ 484 MHz per each microvolt of applied dc voltage. This effect is now well documented, though a direct detection of the Josephson radiation is tricky; it is much easier to observe the *phase locking* (synchronization)¹⁵ of the radiation by external microwave signal, which results in formation of nearly flat dc current steps at dc voltages

$$\bar{V}_n = n \frac{\hbar \omega}{2e}, \quad (2.57)$$

where ω is the external signal frequency and n is an integer.¹⁶ This effect is now being used in highly accurate standards of dc voltage.¹⁷

Now, let us move on to a discussion of the opposite case, when a 1D particle moves in various potential profiles $U(x)$ that are constant in time. Conceptually, the simplest of such profiles is a potential step – see Fig. 4.

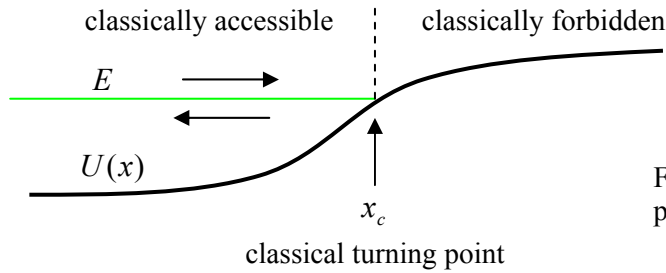


Fig. 2.4. Classical 1D motion in a potential profile $U(x)$.

As I am sure the reader knows, in classical mechanics, if a particle is incident on such a step (in Fig. 4, from the left), its kinetic energy $p^2/2m$ cannot be negative, so that it can only travel through the *classically accessible* region where its (conserved) full energy,

$$E = \frac{p^2}{2m} + U(x), \quad (2.58)$$

is larger than the local value $U(x)$. Let the initial velocity $v = p/m$ be positive, i.e. directed toward the step. Before it has reached the *classical turning point* x_c , defined by equation

$$U(x_c) = E, \quad (2.59)$$

¹⁵ See, e.g., CM Sec. 4.4.

¹⁶ If ω is not too high, this effect may be adequately described combining Eqs. (54)-(55). Let me leave this task for the reader.

¹⁷ The most precise proof that the Josephson frequency-to-voltage ratio f_J/V does not depend on superconducting material (to at least 15 decimal places!) has been carried out by the group led by J. Lukens here at Stony Brook – see J.-S. Tsai *et al.*, *Phys. Rev. Lett.* **51**, 316 (1983).

kinetic energy $p^2/2m$ never turns to zero, so that the particle continues to move in the initial direction. On the other hand, the particle cannot penetrate that *classically forbidden region* $x > x_c$, because there its kinetic energy would be negative there. At the point $x = x_c$, particle's velocity changes sign, i.e. it is reflected back from the classical turning point.

In order to see what the wave mechanics says about this situation, let us start from the simplest, sharp potential step shown with bold black lines in Fig. 5:

$$U(x) = U_0 \theta(x) = \begin{cases} 0, & \text{at } x < 0, \\ U_0, & \text{at } 0 < x. \end{cases} \quad (2.60)$$

For this choice, and any energy within the interval $0 < E < U_0$, the classical turning point is $x_c = 0$.

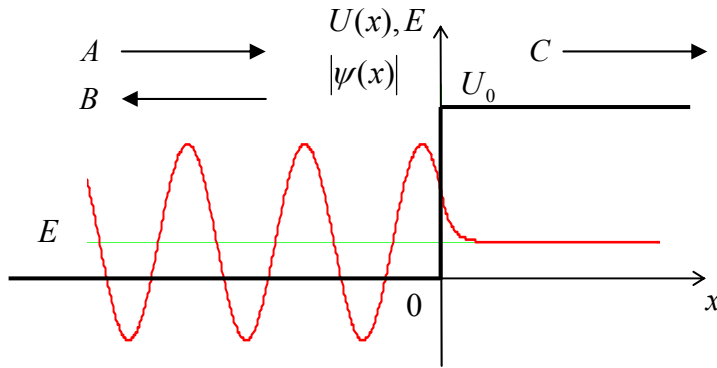


Fig. 2.5. Reflection of a monochromatic wave from a potential step $U_0 > E$. (This particular wavefunction's shape is for $U_0 = 5E$.) The wavefunction is plotted with the same schematic vertical offset by E , as those in Fig. 1.7.

Let us represent an incident particle with a wave packet so long that the spread $\delta k \sim 1/\delta x$ of its wave number spectrum, and hence the energy uncertainty $\delta E = \hbar \delta \omega = \hbar (d\omega/dk) \delta k$ is negligible in comparison with its average value $E < U_0$, as well as with $(U_0 - E)$. In this case, E may be considered a given constant, and the time dependence of the solution is given by Eq. (1.61), and we can limit ourselves to the solution of the 1D version of the stationary Schrödinger equation (1.63), in this case

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U(x) \psi = E \psi, \quad (2.61)$$

for the spatial part $\psi(x)$ of the wavefunction.¹⁸

At $x < 0$, i.e. at $U = 0$, the equation is reduced to the Helmholtz equation (1.75), and may be satisfied with two traveling waves, proportional to $\exp\{+ikx\}$ and $\exp\{-ikx\}$ correspondingly, with k satisfying the dispersion equation (1.30):

$$k^2 \equiv \frac{2mE}{\hbar^2}. \quad (2.62)$$

Thus the general solution of Eq. (61) in this region may be presented as

¹⁸ Note that this is *not* the eigenproblem like the one we have solved in Sec. 1.4 for a quantum well. Indeed, now energy E is considered fixed – e.g., by the initial conditions that launch a long wave packet upon the potential step, from the left.

$$\psi_-(x) = Ae^{+ikx} + Be^{-ikx}. \quad (2.63)$$

Incident and reflected waves

The second term in the right-hand part evidently describes an (infinitely long) wave packet traveling to the left, which represents particle's reflection from the potential step. If $B = -A$, this solution is reduced to Eq. (1.76) for the potential well with infinitely high walls, but as we will see in a minute, for our current case of finite step height U_0 , the relation between coefficients B and A may be different.

To show this, let us solve Eq. (61) for $x > 0$, where $U = U_0 > E$. In this region the equation may be rewritten as

$$\frac{d^2\psi_+}{dx^2} = \kappa^2\psi_+, \quad (2.64)$$

where κ is a real constant defined by the relation similar to Eq. (62):

$$\kappa^2 \equiv \frac{2m(U_0 - E)}{\hbar^2} > 0. \quad (2.65)$$

The general solution of Eq. (64) is the sum of $\exp\{+\kappa x\}$ and $\exp\{-\kappa x\}$, with arbitrary coefficients. However, the wavefunction should be finite at $x \rightarrow \infty$, so only the latter exponent is acceptable:

Decaying wave in classically forbidden region

$$\psi_+(x) = Ce^{-\kappa x}. \quad (2.66)$$

This penetration of the wavefunction into the classically forbidden region, and hence a finite probability to find the particle there, is one of the most fascinating predictions of quantum mechanics, and has been repeatedly observed in experiment, e.g., via tunneling experiments – see below. From Eq. (66), it is evident that the constant κ , defined by Eqs. (65), may be interpreted as the reciprocal penetration depth. Even for the lightest particles this depth is usually very small. Indeed, for $E \ll U_0$ that equation yields

$$\delta \equiv \frac{1}{\kappa} \Big|_{E=0} = \frac{\hbar}{(2mU_0)^{1/2}}. \quad (2.67)$$

For example, for a conduction electron in a typical metal, that runs, at its surface, into a sharp potential step U_0 , whose height equals to metal's workfunction $W \approx 5$ eV (see the discussion of the photoelectric effect in Sec. 1.1), δ is close to 0.1 nm, i.e. is close to a typical size of an atom. For heavier elementary particles (e.g., protons) the penetration depth is correspondingly lower, and for macroscopic bodies it is hardly measurable.

Returning to our problem, we still should find coefficients A , B , and C from the boundary conditions at $x = 0$. Since E is a finite constant, and $U(x)$ is a finite function, Eq. (61) says that $d^2\psi/dx^2$ should be finite as well. This means that the first derivative should be continuous:

$$\lim_{\varepsilon \rightarrow 0} \left(\frac{d\psi}{dx} \Big|_{x=+\varepsilon} - \frac{d\psi}{dx} \Big|_{x=-\varepsilon} \right) = \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{+\varepsilon} \frac{d^2\psi}{dx^2} dx = \frac{2m}{\hbar^2} \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{+\varepsilon} [U(x) - E] \psi dx = 0. \quad (2.68)$$

Repeating such calculation for function $\psi(x)$ itself, we see that it also should be continuous at all points, including $x = 0$, so that

$$\psi_-(0) = \psi_+(0), \quad \frac{d\psi_-}{dx}(0) = \frac{d\psi_+}{dx}(0). \quad (2.69)$$

Plugging solutions (63) and (66) into these two boundary conditions, we get a system of two linear equations

$$A + B = C, \quad ikA - ikB = -\kappa C, \quad (2.70)$$

whose (elementary) solution enables us to express B and C via A :

$$B = A \frac{k - i\kappa}{k + i\kappa}, \quad C = A \frac{2k}{k + i\kappa}. \quad (2.71)$$

We immediately see that since the nominator and denominator in the first of these formulas have equal moduli, so that $|B| = |A|$. This means that, as we could expect, a particle with energy $E < U_0$ is totally reflected from the step. As a result, at $x < 0$ our solution (63) may be presented by a standing wave

$$\psi_- = 2iAe^{i\theta} \sin(kx - \theta), \quad \text{with } \theta \equiv \arctan \frac{k}{\kappa}. \quad (2.72)$$

Notice that the shift $\Delta x \equiv \theta/k = (\arctan k/\kappa)/k$ of the standing wave to the right, due to the partial penetration of the wavefunction under the potential step, is commensurate with, but generally not equal to $\delta \equiv 1/\kappa$. Figure 5 shows the full behavior of the wavefunction, for a particular case $E = U_0/5$, at which $k/\kappa = [E/(U_0 - E)]^{1/2} = 1/2$.

According to Eq. (65), as the particle's energy E is increased to approach U_0 , the penetration depth $1/\kappa$ diverges. This raises an important issue: what happens at $E > U_0$, i.e. if there is no classically forbidden region in the problem? Again, in classical mechanics the incident particle would continue to move to the right, though with a reduced velocity, corresponding to the new kinetic energy $E - U_0$, so there would be no reflection. In quantum mechanics, however, the situation is different. In order to analyze it, it is not necessary to re-solve the whole problem; it is sufficient to note that all our calculations, and hence Eqs. (71) are still valid if we take¹⁹

$$\kappa = -ik', \quad \text{with } k'^2 \equiv \frac{2m(E - U_0)}{\hbar^2} > 0. \quad (2.73)$$

With this replacement, Eq. (71) becomes²⁰

$$B = A \frac{k - k'}{k + k'}, \quad C = A \frac{2k}{k + k'}. \quad (2.74)$$

The most important result of this change is that now the reflection is *not* complete: $|B| < |A|$. In order to evaluate this effect qualitatively, it is more fair to use not the B/A or C/A ratios, but rather that

¹⁹ Our earlier discarding of the particular solution $\exp\{\kappa x\}$, now becoming $\exp\{-ik'x\}$, is still valid, but now on a different grounds: this term would describe a wave packet incident on the potential step from the right, and this is not the problem under our consideration.

²⁰ These formulas are completely similar to those for the partial reflection of classical waves from a sharp interface between two uniform media, at normal incidence (see, e.g., CM Sec. 5.4 and EM Sec. 7.4), with the effective impedance Z of de Broglie waves proportional to their wave number k .

of the probability currents (5) corresponding to traveling waves with amplitudes C and A , in the corresponding regions (respectively, $x > 0$ and $x < 0$):

$$T \equiv \frac{I_C}{I_A} = \frac{k'|C|^2}{k|A|^2} = \frac{4kk'}{(k+k')^2} = \frac{4[E(E-U_0)]^{1/2}}{[E^{1/2} + (E-U_0)^{1/2}]^2}. \quad (2.75)$$

Potential
step's
transmission

(T so defined is called the *transparency* of the inhomogeneity, in our current case of the potential step.) The result given by Eq. (75) is plotted in Fig. 6a. Notice its most important features:

- (i) At $U_0 = 0$, the transparency is full, $T = 1$ – naturally, for having no step at all.
- (ii) At $U_0 \rightarrow E$, the transparency tends to zero – giving a proper connection with the case $E < U_0$.
- (iii) We can use result (75) even for $U_0 < 0$, i.e. for the *step-down* (or “cliff”) profile – see Fig. 6b. Very counter-intuitively, the particle is (partly) reflected even from such a cliff, and the transmission diminishes (rather slowly) at $U_0 \rightarrow -\infty$.

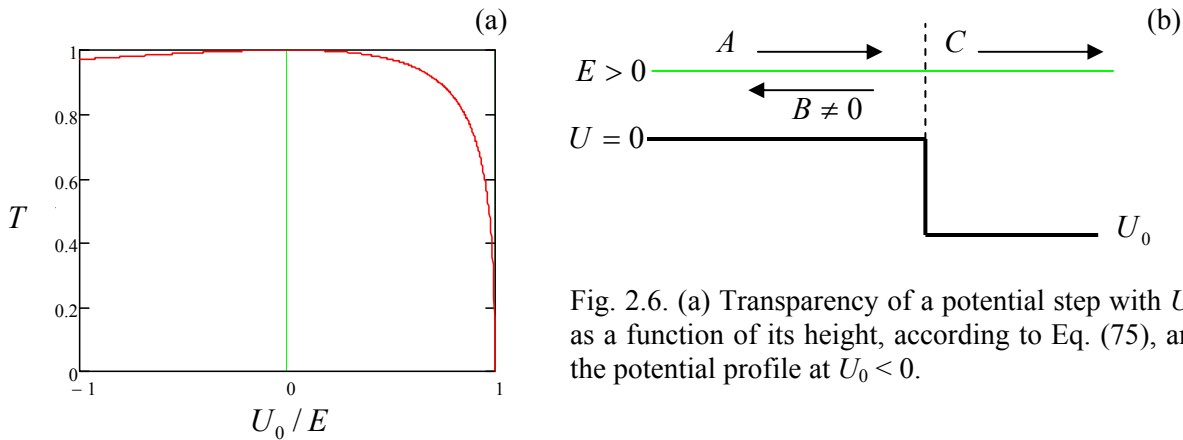


Fig. 2.6. (a) Transparency of a potential step with $U_0 < E$ as a function of its height, according to Eq. (75), and (b) the potential profile at $U_0 < 0$.

The most important conceptual conclusion of our analysis is that the quantum particle is *partly reflected* from a potential step with $U_0 < E$, in the sense that there is a nonvanishing probability $T < 1$ to find it passed over the step, while there is also probability $(1 - T)$ to have it reflected.

The same property is exhibited, for *any* relation between E and U_0 , by another simple potential profile $U(x)$, the famous *tunnel barrier*. Figure 7 shows its simple, “rectangular” version:

$$U(x) = \begin{cases} 0, & \text{for } x < -d/2, \\ U_0, & \text{for } -d/2 < x < +d/2, \\ 0, & \text{for } +d/2 < x. \end{cases} \quad (2.76)$$

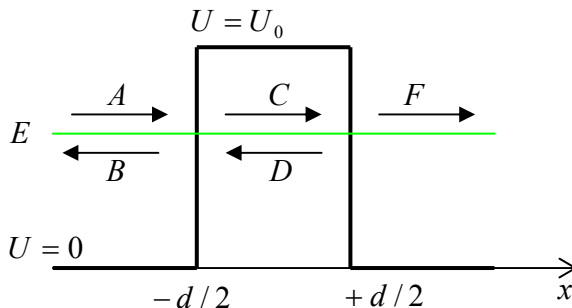


Fig. 2.7. Rectangular tunnel barrier.

In order to analyze this problem, it is sufficient to look for the solution to the Schrödinger equation in the form (63) at $x \leq -d/2$. At $x > +d/2$, i.e., behind the barrier, we may use the arguments presented above (no wave packet source on the right!) to keep just one traveling wave,

$$\psi_+(x) = Fe^{ikx}. \quad (2.77)$$

However, under the barrier, i.e. at $-d/2 \leq x \leq +d/2$, we should generally keep both exponential terms,

$$\psi_b(x) = Ce^{-\kappa x} + De^{+\kappa x}, \quad (2.78)$$

because our previous argument, used in the potential step problem's solution, is no longer valid. (Here k and κ are still defined, respectively, by Eqs. (62) and (65).) In order to find the relation between coefficients A , B , C , D , and F , we need to plug in the solutions into the boundary conditions similar to Eqs. (69), but now at two boundary points, $x = \pm d/2$.

Solving the resulting system of 4 linear equations for five amplitudes (A , B , C , D , and F), we can readily calculate four ratios B/A , C/A , etc., in particular,

$$\frac{F}{A} = \frac{\exp\{-ikd\}}{\cosh \kappa d + \frac{i}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \sinh \kappa d}, \quad (2.79a)$$

and hence barrier's transparency

$$T \equiv \left| \frac{F}{A} \right|^2 = \left[\cosh^2 \kappa d + \left(\frac{\kappa^2 - k^2}{2\kappa k} \right)^2 \sinh^2 \kappa d \right]^{-1}. \quad (2.79b)$$

Figure 8a shows the transparency as a function of particle energy E , for several characteristic values of the barrier thickness d , or rather of the ratio d/δ , where δ is defined by Eq. (67).

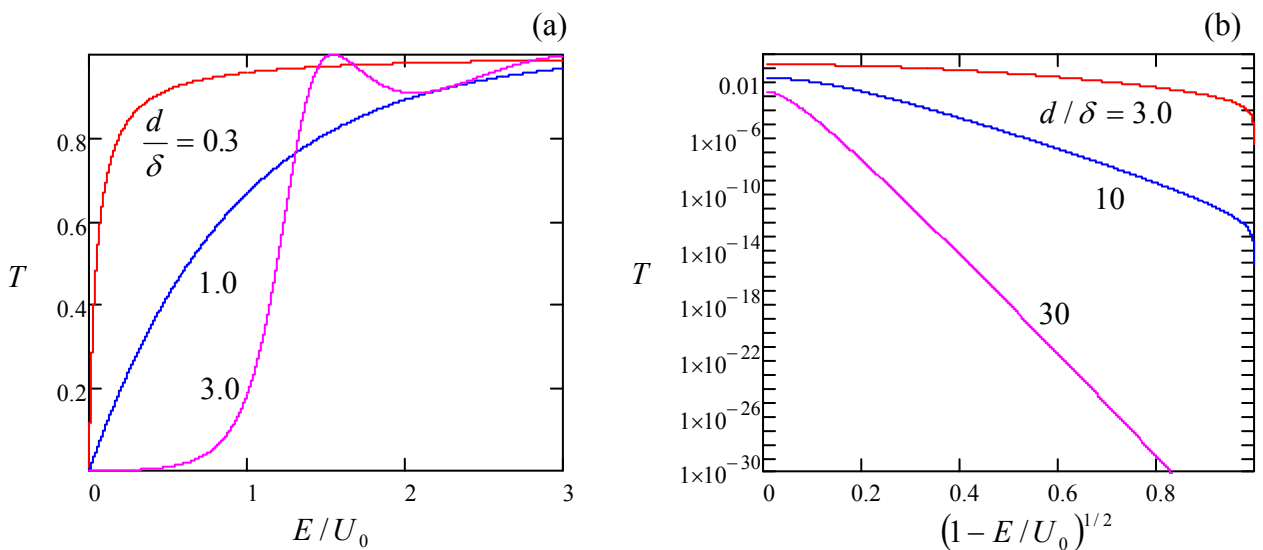


Fig. 2.8. Transparency of the rectangular tunnel barrier as a function of particle's energy E .

The plots show that for a thin barrier ($d < \delta$) the transparency grows gradually with particle's energy. This growth is natural, because the penetration constant κ decreases with the growth of E , i.e., the wavefunction penetrates more and more into the barrier, so that more and more of it is “picked up” at the second interface ($x = +d/2$) and transferred into the wave $F\exp\{ikx\}$ propagating behind the barrier. As Eq. (79b) shows, for thick barriers ($d \gg \delta$), this dependence is dominated by an exponent,

$$T \approx \left(\frac{4k\kappa}{k^2 + \kappa^2} \right)^2 e^{-2\kappa d}, \quad (2.80)$$

Thick
tunnel
barrier's
transparency

that may be clearly seen as a straight segments in semi-log plots (Fig. 8b) of T as a function of the combination $(1 - E/U_0)^{1/2}$ which is proportional to κ - see Eq. (65).

Equation (80) also clearly shows the exponential dependence of the barrier transparency of its thickness at $d \gg \delta$. This dependence is the most important factor for various applications of the quantum-mechanical tunneling – from the field emission²¹ of electrons to scanning tunneling microscopy.²² Also noted should be substantial negative implications of the effect for modern electronic engineering, most importantly imposing a limit for scaling down of field effect transistors in semiconductor integrated circuits (and hence the circuit density increase according to the well-known Moore's law), due to increase of tunneling both through the gate oxide and along transistor's channel.²³

Another interesting effect visible in Fig. 8a (for case $d = 0.3\delta$) are the oscillations of T at $E > U_0$. This is our first glimpse at one more interesting quantum effect: *resonant tunneling*. I will discuss this effect in detail in Sec. 5 below.

2.4. The WKB approximation

Before moving on to exploring more complex potentials, let us see whether the results discussed in the previous section hold on in the opposite limit of so-called *soft*, gradual potential profiles, like that sketched in Fig. 4. (The quantitative conditions of the “softness” will be derived below). The most efficient analytical tool in this limit is the *WKB* (or “quasiclassical”) *approximation* developed by H. Jeffrey, G. Wentzel, A. Kramers, and L. Brillouin in 1926-27.

In order to derive its 1D version, let us rewrite the Schrödinger equation (61) as

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi = 0 \quad (2.81)$$

where the local value of wave number $k(x)$ is defined similarly to Eq. (73),

$$k^2(x) \equiv \frac{2m[E - U(x)]}{\hbar^2}; \quad (2.82)$$

Local
wave
number

but now it may be a function of x . We already know that for $k(x) = \text{const}$, the fundamental solutions of this equation have form $A\exp\{+ikx\}$ and $B\exp\{-ikx\}$. Any of them may be presented in a simple form

²¹ See, e.g., G. Fursey, *Field Emission in Vacuum Microelectronics*, Kluwer, New York, 2005.

²² See, e.g., G. Binnig and H. Rohrer, *Helv. Phys. Acta* **55**, 726 (1982).

²³ See, e.g., V. Sverdlov *et al.*, *IEEE Trans. on Electron Devices* **50**, 1926 (2003).

$$\psi(x) = e^{i\Phi(x)}, \quad (2.83)$$

where $\Phi(x)$ is a complex function, in this simplest case equal to either $(kx - i\ln A)$ or $(-kx - i\ln B)$. This is why we may try use Eq. (83) to look for solution of Eq. (81) even in the general case, $k(x) \neq \text{const}$. Differentiating Eq. (83) twice, we get

$$\frac{d\psi}{dx} = i \frac{d\Phi}{dx} e^{i\Phi}, \quad \frac{d^2\psi}{dx^2} = \left[i \frac{d^2\Phi}{dx^2} - \left(\frac{d\Phi}{dx} \right)^2 \right] e^{i\Phi}. \quad (2.84)$$

Plugging the last expression into Eq. (81) and requiring the factor before $\exp\{i\Phi(x)\}$ to vanish, we get

$$i \frac{d^2\Phi}{dx^2} - \left(\frac{d\Phi}{dx} \right)^2 + k^2(x) = 0. \quad (2.85)$$

This is still an exact, general result. At the first sight, it looks worse than the initial equation (81), because Eq. (85) is nonlinear. However, it is more ready for simplification in the limit when the potential profile is very smooth, $dU/dx \rightarrow 0$. Indeed, we know that for a uniform potential, $\Phi'' = 0$. Hence, in the “0th” approximation, $\Phi(x) \rightarrow \Phi_0(x)$, we may try to keep that result, so that Eq. (85) yields

$$\left(\frac{d\Phi_0}{dx} \right)^2 = k^2(x). \quad (2.86a)$$

Just as in the uniform case, this equation has two roots,

$$\frac{d\Phi_0}{dx} = \pm k(x), \quad (2.86b)$$

so that its general solution is

$$\psi_0(x) = A \exp \left\{ +i \int^x k(x') dx' \right\} + B \exp \left\{ -i \int^x k(x') dx' \right\}, \quad (2.87)$$

where x' is the lower limits of integration affect only constants A and B . The physical sense of this result is simple: it is a sum of forward- and back-propagating waves, with the coordinate-dependent local wave number $k(x)$ that self-adjusts to the potential profile.

Let me emphasize the non-trivial nature of this approximation.²⁴ First, any attempt to address the problem with a standard perturbation approach (say, $\psi = \psi_0 + \psi_1 + \dots$, with ψ_n proportional to n^{th} power of some small parameter,²⁵ in this case scaling d^2U/d^2x) would fail for most potentials, because even a slight but persisting deviation of $U(x)$ from a constant leads to a gradual accumulation of phase Φ_0 , impossible to describe by any small perturbation of ψ . Second, the dropping of term $d^2\Phi/dx^2$ in Eq. (85) is not too easy to justify. Indeed, since we are committed to the “soft potential limit” $dU/dx \rightarrow 0$, we should be ready to assume the characteristic length a of spatial variation of Φ to be large, and neglect

²⁴ Philosophically, this space-domain method is very close to the time-domain *rotating wave approximation* (RWA) used, for example, in the classical and quantum theory of oscillations – see, e.g., CM Secs. 4.2-4.5, and Secs. 6.5, 7.6, 7.7, 9.2, and 9.4 of this course.

²⁵ Such perturbation theories will be discussed in Chapter 6.

the terms that are the smallest ones in the limit $a \rightarrow \infty$. However, both first terms in Eq. (85) are apparently of the same order in a , namely $O(a^{-2})$; why have we neglected just one of them?

The price we have paid for such a “sloppy” treatment is high: Eq. (87) does *not* satisfy the fundamental property of the Schrödinger equation, the probability current conservation. Indeed, since Eq. (81) describes a fixed-energy (stationary) spatial part of the general Schrödinger equation, its probability density $w = \Psi\Psi^* = \psi\psi^*$, and should not depend on time. Hence, according to Eq. (6), we should have $I(x) = \text{const}$. However, this is not true for each component of Eq. (87); for example for the forward-propagating component of its right-hand part, Eq. (5) yields

$$I_0(x) = \frac{\hbar}{m} |A|^2 k(x), \quad (2.88)$$

evidently not a constant if $k(x) \neq \text{const}$.

The brilliance of the WKB theory is that the problem may be fixed without revising the 0th approximation. Indeed, let us explore the next, 1st approximation instead:

$$\Phi(x) \rightarrow \Phi_{\text{WKB}}(x) \equiv \Phi_0(x) + \Phi_1(x), \quad (2.89)$$

where Φ_0 still obeys Eq. (85), while Φ_1 describes a small correction to the 0th approximation, in the following sense:²⁶

$$\left| \frac{d\Phi_1}{dx} \right| \ll \left| \frac{d\Phi_0}{dx} \right| = k(x). \quad (2.90)$$

Plugging Eq. (89) into Eq. (85), with the account of the definition (86), we get

$$i \left(\frac{d^2\Phi_0}{dx^2} + \frac{d^2\Phi_1}{dx^2} \right) - \frac{d\Phi_1}{dx} \left(2 \frac{d\Phi_0}{dx} + \frac{d\Phi_1}{dx} \right) = 0. \quad (2.91)$$

Using condition (90), we may neglect $d^2\Phi_1/dx^2$ in comparison with $d^2\Phi_0/dx^2$ in the first parenthesis, and $d\Phi_1/dx$ in comparison with $2d\Phi_0/dx$ in the second parenthesis. As a result, we get the following *approximate* result:

$$\frac{d\Phi_1}{dx} = \frac{i}{2} \frac{d^2\Phi_0}{dx^2} / \frac{d\Phi_0}{dx} = \frac{i}{2} \frac{d}{dx} \left(\ln \frac{d\Phi_0}{dx} \right) = \frac{i}{2} \frac{d}{dx} [\ln k(x)] = i \frac{d}{dx} [\ln k^{1/2}(x)], \quad (2.92)$$

$$i\Phi|_{\text{WKB}} \equiv i\Phi_0 + i\Phi_1 = \pm i \int^x k(x') dx' + \ln \frac{1}{k^{1/2}(x)}, \quad (2.93)$$

$$\psi_{\text{WKB}}(x) = \frac{a}{k^{1/2}(x)} \exp \left\{ i \int^x k(x') dx' \right\} + \frac{b}{k^{1/2}(x)} \exp \left\{ -i \int^x k(x') dx' \right\}, \quad \text{for } k^2(x) > 0. \quad (2.94)$$

WKB
wave-
function

(Again, the lower integration limit is arbitrary, but its choice may be incorporated into complex constants a and b .) This modification of the 0th approximation (87) overcomes the problem of current continuity; for example, for the forward-propagating wave, Eq. (5) gives

²⁶ For certainty, I will use the discretion given by Eq. (82) to define $k(x)$ as the *positive* root of its right-hand part.

WKB
probability
current

$$I_{\text{WKB}}(x) = \frac{\hbar}{m} |a|^2 = \text{const.} \quad (2.95)$$

Physically, factor $k^{1/2}$ in the denominator of the WKB wavefunction's pre-exponent is easy to understand. The smaller the local group velocity (34) of the wave packet, $v_{\text{gr}}(x) = \hbar k(x)/m$, the “easier” (more probable) it should be to find the particle within a certain interval dx . This is exactly the result that WKB gives: $dW/dx = w(x) = \psi\psi^* \propto 1/k(x) \propto 1/v_{\text{gr}}$.

Another value of the 1st approximation is a clarification of WKB theory's validity condition: it is given by Eq. (90). Plugging into this relation the first form of Eq. (92), and estimating $|\Phi_0'|$ as $|\Phi_0'|/a$, where a is the spatial scale of a substantial change of $|\Phi_0'| = k(x)$, we can rewrite the condition as

$$ka \gg 1. \quad (2.96)$$

WKB:
first
condition
of validity

In plain English, this means that the region where $U(x)$, and hence $k(x)$, change substantially should contain many de Broglie wavelengths $\lambda = 2\pi/k$.

So far I have implied that $k^2(x) \propto E - U(x)$ is positive, i.e. particle moves in the classically accessible region. Now let us extend the WKB approximation to the situation where the difference $E - U(x)$ may change sign, for example to the reflection problem sketched in Fig. 4. Just as we did for the sharp potential step, we first need to find the appropriate solution for the classically forbidden region, in this case $x > x_c$. For that, there is no need to redo our calculations, because they are still valid if we, just as in the sharp step problem, take $k(x) = i\kappa(x)$, where

$$\kappa^2(x) \equiv \frac{2m[U(x) - E]}{\hbar^2} > 0, \quad \text{for } x > x_c, \quad (2.97)$$

and keep just one of two possible solutions (with $\kappa > 0$), in analogy with Eq. (66). The result is

$$\psi_{\text{WKB}}(x) = \frac{c}{\kappa^{1/2}(x)} \exp\left\{-\int_{x_c}^x \kappa(x') dx'\right\}, \quad \text{for } k^2 < 0, \text{ i.e. } \kappa^2 > 0, \quad (2.98)$$

with the lower limit at some point with $\kappa^2 > 0$ as well. This is a really wonderful formula! It describes the quantum-mechanical penetration of the particle into the classically forbidden region, and provides a natural generalization of Eq. (66) - leaving intact, of course, our estimates of the depth $\delta \sim 1/\kappa$ of such penetration.

Now we have to do what we have done for the sharp-step problem in Sec. 2: use the boundary conditions in the interface point $x = x_c$ to relate constants a , b , and c . However, now this operation is a tad more complex, because both WKB functions (94) and (98) diverge, albeit weakly, at the classical turning point, where both $k(x)$ and $\kappa(x)$ tend to zero. This *connection problem* may be however, solved in the following way.²⁷ Let us use the commitment of potential “softness”, assuming that it allows us to keep just two leading terms in the Taylor expansion of function $U(x)$ at point x_c :

$$U(x) \approx U(x_c) + \frac{dU}{dx}\bigg|_{x=x_c} (x - x_c) = E + \frac{dU}{dx}\bigg|_{x=x_c} (x - x_c). \quad (2.99)$$

²⁷ An alternative way to solve the connection problem, without involving the Airy functions but using an analytical extension of WKB formulas to the plane of complex argument, may be found, e.g., in Sec. 47 of textbook by L. Landau and E. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory*, 3rd ed. Pergamon, 1977.

Using this truncated expansion, and introducing a dimensionless variable for coordinate's deviation from the classical turning point,

$$\zeta \equiv \frac{x - x_c}{x_0}, \quad x_0 \equiv \left(\frac{\hbar^2}{2m(dU/dx)} \right)^{1/3}, \quad (2.100)$$

we reduce the Schrödinger equation (61) to the simple *Airy equation*

$$\frac{d^2\psi}{d\zeta^2} - \zeta\psi = 0. \quad (2.101) \quad \text{Airy equation}$$

As for all linear, ordinary differential equations of the second order, the general solution of Eq. (101) may be presented as a linear combination of two fundamental solutions, in this case called *Airy functions* $\text{Ai}(\zeta)$ and $\text{Bi}(\zeta)$, shown in Fig. 9a.

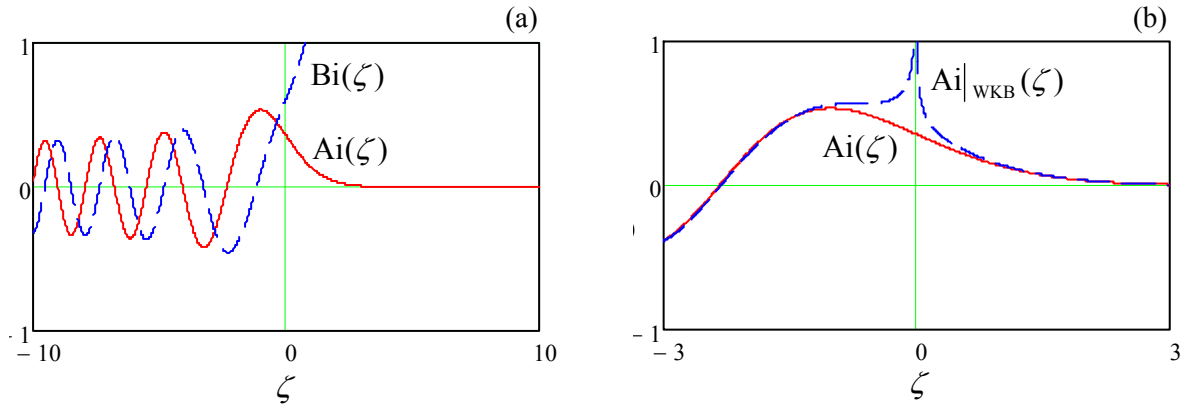


Fig. 2.9. (a) Airy functions Ai and Bi , and (b) the WKB approximation for function $\text{Ai}(\zeta)$.

The latter function diverges at $\zeta \rightarrow \infty$, and thus is not suitable for our current problem (Fig. 4), while the former function has the following asymptotic behaviors at $|\zeta| \gg 1$:²⁸

$$\text{Ai}(\zeta) \rightarrow \frac{1}{\pi^{1/2}|\zeta|^{1/4}} \times \begin{cases} \frac{1}{2} \exp\left\{-\frac{2}{3}\zeta^{3/2}\right\}, & \text{for } \zeta \rightarrow +\infty, \\ \sin\left\{\frac{2}{3}(-\zeta)^{3/2} + \frac{\pi}{4}\right\}, & \text{for } \zeta \rightarrow -\infty. \end{cases} \quad (2.102)$$

Now let us apply the WKB approximation to the Airy equation (101). Taking the classical turning point ($\zeta = 0$) for the lower limit, for $\zeta > 0$ we get (in dimensionless units)

²⁸ The following (exact!) integral formulas,

$$\text{Ai}(\zeta) = \frac{1}{\pi} \int_0^\infty \cos\left(\frac{\xi^3}{3} + \zeta\xi\right) d\xi, \quad \text{Bi}(\zeta) = \frac{1}{\pi} \int_0^\infty \left[\exp\left\{-\frac{\xi^3}{3} + \zeta\xi\right\} \sin\left(\frac{\xi^3}{3} + \zeta\xi\right) \right] d\xi,$$

are often convenient for practical calculation of Airy functions at intermediate values of the argument, $|\zeta| \sim 1$.

$$\kappa^2(\zeta) = \zeta, \quad \kappa(\zeta) = \zeta^{1/2}, \quad \int_0^\zeta \kappa(\zeta') d\zeta' = \frac{2}{3} \zeta^{3/2}, \quad (2.103)$$

i.e. exactly the exponent in the first line of Eq. (102). Making a similar calculation for $\zeta < 0$, with the natural assumption $|b| = |a|$ (full reflection from the potential step), we arrive at the following result:

$$\text{Ai}_{\text{WKB}}(\zeta) = \frac{1}{|\zeta|^{1/4}} \times \begin{cases} c \exp\left\{-\frac{2}{3} \zeta^{3/2}\right\}, & \text{for } \zeta > 0, \\ a \sin\left\{\frac{2}{3}(-\zeta)^{3/2} + \varphi\right\}, & \text{for } \zeta < 0. \end{cases} \quad (2.104)$$

This approximation differs from the exact solution at small values of ζ , i.e. close to the classical turning point – see Fig. 9b. However, at $|\zeta| \gg 1$, Eqs. (104) describe the Airy function exactly if

$$\varphi = \frac{\pi}{4} \quad \text{and} \quad c = \frac{a}{2}. \quad (2.105)$$

Hence we can use these *connection formulas* to express the relations between coefficients a , b , and c of the general WKB solutions (94) and (98). In particular, the first of them yields $b = -a \exp\{i\pi/2\}$, so that Eq. (94) becomes

$$\psi_{\text{WKB}}(x < x_c) = \frac{a'}{k^{1/2}(x)} \left[\exp\left\{i \int_{x_c}^x k(x') dx'\right\} - \exp\left\{-i \int_{x_c}^x k(x') dx' + i \frac{\pi}{2}\right\} \right]. \quad (2.106)$$

This result may be also described by a simple mnemonic rule: reflecting from a “soft” potential step, the wavefunction acquires an additional phase shift $\Delta\varphi = \pi/2$, if compared with the reflection from a “hard” (vertical) potential wall located at $x = x_c$, for which, according to Eq. (1.76), we would have $b = -a$.

Let us quantify the condition of validity of the connection formulas (105) - in other words, the criterion of the step “softness”. For that, within the region where the WKB approximation differs from for the exact Airy equation ($|\zeta| \sim 1$, i.e. $|x - x_c| \sim x_0$), the deviation from the linear approximation (99) of the potential profile should be relatively small. This deviation may be estimated using the next term of the Taylor expansion, $d^2U/d^2x|_{x=x_c}(x - x_c)^2/2$. As a result, the softness condition may be expressed as $|d^2U/d^2x|_{x=x_c} x_0 \ll |dU/dx|_{x=x_c}$. With the account of Eq. (100) for x_0 , the condition becomes

$$\left| \frac{d^2U}{dx^2} \right|_{x=x_c}^3 \ll \frac{2m}{\hbar^2} \left(\frac{dU}{dx} \right)_{x=x_c}^4, \quad (2.107)$$

WKB:
second
condition
of validity

As an example of a very useful application of the WKB approximation, let us use it to calculate the energy spectrum of 1D particle in a soft 1D quantum well (Fig. 10). As was discussed above, we may always consider the standing wave describing an eigenstate ψ_n (corresponding to eigenenergy E_n) as a traveling wave going back and forth between the walls, being sequentially reflected by each of them. Let us apply the WKB approximation to such a traveling wave. First, according to Eq. (94), propagating from the left classical turning point x_L to the right point x_R , it acquires phase change

$$\Delta\varphi_{\rightarrow} = \int_{x_L}^{x_R} k(x) dx. \quad (2.108)$$

At the reflection from the soft wall at x_R , according to the connection formula (106), the wave acquires an additional shift $\pi/2$. Now, traveling back from x_R to x_L the wave gets a shift similar to one given by Eq. (108): $\Delta\varphi_{\leftarrow} = \Delta\varphi_{\rightarrow}$. Finally, at the reflection from x_L it gets one more $\pi/2$. Summing up all these contributions, we may write the self-consistency condition (that the wavefunction “catches its own tail with its teeth”), in the form

$$\Delta\varphi_{\text{total}} \equiv \Delta\varphi_{\rightarrow} + \frac{\pi}{2} + \Delta\varphi_{\leftarrow} + \frac{\pi}{2} = 2 \int_{x_L}^{x_R} k(x) dx + \pi = 2\pi n, \quad \text{with } n = 1, 2, \dots \quad (2.109)$$

Rewriting this result in terms of particle's momentum $p(x) = \hbar k(x)$, we arrive at the famous 1D *Bohr-Sommerfeld quantization rule*

$$\oint_C p(x) dx = 2\pi\hbar \left(n - \frac{1}{2} \right), \quad (2.110)$$

Bohr-Sommerfeld
quantization
rule

where the closed path C means the full period of classical motion.²⁹

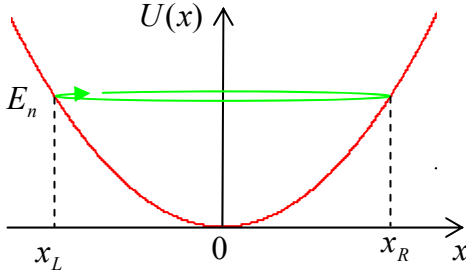


Fig. 2.10. Quasiclassical treatment of eigenstates in a soft 1D potential well.

Let us see what does this rule give for the very important particular case of a quadratic potential profile of a harmonic oscillator of frequency ω_0 . In this case,

$$U(x) = \frac{m}{2} \omega_0^2 x^2, \quad (2.111)$$

and the classical turning points are the roots of a simple equation

$$\frac{m}{2} \omega_0^2 x_c^2 = E_n, \quad (2.112)$$

so that $x_R = x_n \equiv (2E_n/m)^{1/2}/\omega_0 > 0$, $x_L = -x_n < 0$. Due to potential's symmetry, the integration required by Eq. (110) is also simple:

$$\int_{x_L}^{x_R} p(x) dx = \int_{-x_c}^{+x_c} \{2m[E_n - U(x)]\}^{1/2} dx = (2mE_n)^{1/2} \int_{-x_c}^{+x_c} \left(1 - \frac{x^2}{x_n^2}\right)^{1/2} dx = (2mE_n)^{1/2} x_n \frac{\pi}{2} = \frac{2E_n}{\omega_0} \frac{\pi}{2}, \quad (2.113)$$

²⁹ Note that at motion in more than one dimension, a closed classical trajectory may have no turning points. In this case, the constant $\frac{1}{2}$ in the parentheses of Eq. (109), arising from the turns, should be dropped. The simplest example is the circular motion of the electron about the proton in Bohr's picture of the hydrogen atom, for which the modified quantization (109) condition takes form (1.10) postulated by N. Bohr. (A similar relation for the radial motion is sometimes called the *Sommerfeld-Wilson quantization rule*.)

Harmonic
oscillator's
energy
levels

so that Eq. (110) is satisfied if

$$E_n = \hbar\omega_0 \left(n' + \frac{1}{2} \right), \quad \text{with } n' \equiv n - 1 = 0, 1, 2, \dots \quad (2.114)$$

In order to estimate the validity of this result, we have to check condition (96) at all points of the classically allowed region, and Eq. (107) at the turning points. A straightforward calculation shows that both conditions are valid for $n \gg 1$. However, we will see below that Eq. (114) is actually *exactly correct for all energy levels* – thanks to special properties of potential profile (111).

Now, let us look at the second of connection formulas (105), $c = a/2$. Again, it differs from the result (71) for a sharp potential step, that may be rewritten as

$$C = A \frac{2k}{k + i\kappa} = A \frac{2}{[1 + (\kappa/k)^2]^{1/2}} \exp\{-i2\theta\}, \quad (2.115)$$

by both the modulus and phase factor. (In the WKB approximation, the latter factor always equals $\pi/4$.) Hence, again, the WKB approximation's prediction is not exact for sharp potentials; nevertheless, it is broadly used for practical calculations. One of the most important of them is the transparency of an arbitrary but smooth potential barrier (Fig. 11).

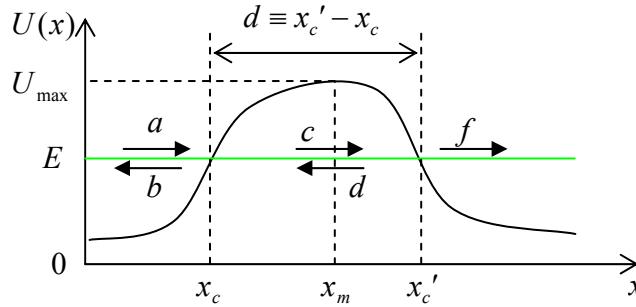


Fig. 2.11. 1D potential barrier of an arbitrary (but smooth) shape.

Here, just as in the case of a rectangular barrier, we need to take into consideration five partial “waves” (or rather fundamental solutions of the Schrödinger equation):³⁰

$$\psi_{\text{WKB}} = \begin{cases} \frac{a}{k^{1/2}(x)} \exp\left\{i \int^x k(x') dx'\right\} + \frac{b}{k^{1/2}(x)} \exp\left\{-i \int^x k(x') dx'\right\}, & \text{for } x < x_c, \\ \frac{c}{\kappa^{1/2}(x)} \exp\left\{-\int^x \kappa(x') dx'\right\} + \frac{d}{\kappa^{1/2}(x)} \exp\left\{\int^x \kappa(x') dx'\right\}, & \text{for } x_c < x < x'_c, \\ \frac{f}{k^{1/2}(x)} \exp\left\{i \int^x k(x') dx'\right\}, & \text{for } x'_c < x, \end{cases} \quad (2.116)$$

where lower limits of integrals are arbitrary (each within the corresponding range of x). Since on the right of the left classical point we have two exponents rather than one, and on the right of the second

³⁰ Sorry, but the same letter, d , is used here for the barrier thickness (defined in this case as the classically forbidden region length, $x'_c - x_c$), and the constant in one of the wave amplitudes – see Eq. (116). Let me hope that the difference between these uses is absolutely evident from the context.

point, one traveling waves rather than two, the connection formulas (105) have to be generalized, using asymptotic formulas not only for $\text{Ai}(\zeta)$, but also for the second Airy function, $\text{Bi}(\zeta)$. The analysis, absolutely similar to that carried out above (though naturally a bit more bulky),³¹ gives a remarkably simple result:

$$T_{\text{WKB}} \equiv \left| \frac{f}{a} \right|^2 = \exp \left\{ -2 \int_{x_c}^{x'_c} \kappa(x) dx \right\} = \exp \left\{ -\frac{2}{\hbar} \int_{x_c}^{x'_c} (2m[U(x) - E])^{1/2} dx \right\}, \quad (2.117)$$

Soft tunnel barrier's transparency

with *no* pre-exponential factor. This formula is broadly used in applied quantum mechanics, despite the approximate character of its pre-exponential coefficient for insufficiently soft barriers that do not satisfy Eq. (107). For example, Eq. (80) shows that for a thick rectangular barrier with $k = \kappa$, i.e. $U_0 = 2E$, the WKB approximation (117) underestimates T by a factor of 4. However, on the logarithmic scale of Fig. 8b, such factor, about half an order of magnitude, still looks as a small correction.

Notice that when E approaches the barrier top U_{max} (Fig. 11), points x_c and x'_c merge, so that, according to Eq. (117), $T_{\text{WKB}} \rightarrow 1$, i.e. the particle reflection vanishes at $E = U_{\text{max}}$. However, this conclusion is incorrect even for smooth barriers where one could naively expect the WKB approximation to work perfectly. Indeed, near point $x = x_m$ where the potential reaches maximum (i.e. $U(x_m) = U_{\text{max}}$), we may always approximate a smooth function $U(x)$ by an inverted parabola,

$$U(x) \approx U_{\text{max}} - \frac{m\omega_0^2(x - x_m)^2}{2}. \quad (2.118)$$

Calculating the derivatives dU/dx and d^2U/dx^2 of this function and plugging them into condition (107), we see that the WKB approximation is only valid if $|U_{\text{max}} - E| \gg \hbar\omega_0$. An exact analysis³² of tunneling through barrier (118) gives the following *Kemble formula*:

$$T = \frac{1}{1 + \exp\{-2\pi(E - U_{\text{max}})/\hbar\omega_0\}}, \quad (2.119)$$

Kemble formula

valid for any sign of difference $(E - U_{\text{max}})$. This formula describes a gradual approach of T to 1, i.e. a *gradual* reduction of reflection at particle energy's increase, with $T = 1/2$ (rather than 1) at $E = U_{\text{max}}$.

Now the last remark of this section: our discussions of the propagator and the WKB approximation open a straight way toward an alternative formulation of quantum mechanics, based on the *Feynman path integral*, but I will postpone its discussion until a more compact (“bra-ket”) notation has been introduced in Chapter 4.

2.5. Transfer matrix, resonant tunneling, and metastable states

Let us now explore motion in more complex potential profiles. The piecewise-constant and smooth-potential models of $U(x)$ are not too convenient here, because they both require “stitching” local

³¹ Note, however, that in the most important case $T_{\text{WKB}} \ll 1$, Eq. (117) may be simply derived from Eqs. (105) – an exercise left for the reader.

³² It was carried out by E. Kemble in 1935. Notice that mathematically the Kemble formula is similar to the Fermi distribution in statistical physics, with effective temperature $T_{\text{ef}} = \hbar\omega_0/2\pi k_B$. This similarity has some interesting implications for the statistics of Fermi gas tunneling.

solutions in each classical turning point, which may lead to very cumbersome calculations. However, we may get a very good insight of the physics phenomena in such profiles, using their approximation by a set of Dirac's delta-functions. For that, let us have a look at what our old result (79) gives in the limit of a very thin and high rectangular barrier, $d \ll \delta$, $E \ll U_0$ (giving $k \ll \kappa \ll 1/d$):

$$T \equiv \left| \frac{F}{A} \right|^2 \rightarrow \frac{1}{|1 + i\alpha|^2} = \frac{1}{1 + \alpha^2}, \quad (2.120)$$

where parameter α is defined as

$$\alpha \equiv \frac{1}{2} \left(\frac{\kappa^2 - k^2}{\kappa k} \right) \kappa d \approx \frac{1}{2} \frac{\kappa^2 d}{k} \approx \frac{m}{\hbar^2 k} U_0 d. \quad (2.121)$$

The last product, $U_0 d$, is just the “area”

$$\mathcal{W} \equiv \int_{U(x) > E} U(x) dx \quad (2.122)$$

of the barrier. This fact implies that the very simple result (120) for the transparency may be correct for a barrier of any shape, provided that it is sufficiently thin and high.

Indeed, let us consider the tunneling problem for a very thin barrier with κd , $\kappa d \ll 1$ (Fig. 12), approximating it by Dirac's δ -function:

$$U(x) = \mathcal{W} \delta(x). \quad (2.123)$$

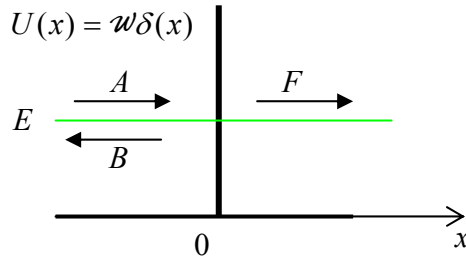


Fig. 2.12. Delta-functional tunnel barrier.

We already know the solutions in all points but $x = 0$ – see Eqs. (63) and (77) – so we only need to analyze boundary conditions in that point to find coefficients A , B , and F – or rather the ratios B/A and F/A . However, due to the special character of the δ -function, we should be careful here. Indeed, instead of Eq. (68) we now get

$$\frac{d\psi_+}{dx}(0) - \frac{d\psi_-}{dx}(0) = \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{+\varepsilon} \frac{d^2\psi}{dx^2} dx = \lim_{\varepsilon \rightarrow 0} \frac{2m}{\hbar^2} \int_{-\varepsilon}^{+\varepsilon} [U(x) - E] \psi dx = \frac{2m}{\hbar^2} \mathcal{W} \psi(0). \quad (2.124)$$

On the other hand, the wavefunction itself is still continuous:

$$\psi_+(0) - \psi_-(0) = \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{+\varepsilon} \frac{d\psi}{dx} dx = 0. \quad (2.125)$$

Using these boundary conditions, we readily get the following system of two linear equations,

$$A + B = F, \quad ikF - (ikA - ikB) = \frac{2m\mathcal{W}}{\hbar^2} F, \quad (2.126)$$

whose solution yields

$$\frac{B}{A} = \frac{-i\alpha}{1+i\alpha}, \quad \frac{F}{A} = \frac{1}{1+i\alpha}, \quad \text{where } \alpha \equiv \frac{m\mathcal{W}}{\hbar^2 k}. \quad (2.127)$$

For the barrier transparency $T \equiv |F/A|^2$, this result again gives Eq. (120). That formula may be recast to give a simple expression (valid only for $E \ll U_{\max}$) for the transmission coefficient,

$$T = \frac{1}{1 + \alpha^2} = \frac{E}{E + E_0}, \quad \text{where } E_0 \equiv \frac{m\mathcal{W}^2}{2\hbar^2}, \quad (2.128)$$

Thin
barrier's
transparency

that shows that as energy becomes larger than parameter E_0 , the barrier's transparency approaches unity.

However, the most important application of Eqs. (126) is for deriving transparency of more complex potential profiles. For that, let us first introduce very general notions of the *scattering* and *transfer matrices*, currently for the 1D case. Consider an arbitrary but finite-length potential “bump” (more formally called a *scatterer*), localized somewhere between points x_1 and x_2 , on the flat potential background, say $U = 0$ (Fig. 13). We know the general solution, with a certain energy E , outside the interval are a set of two sinusoidal waves. Let us present them in the form

$$\psi_j = A_j e^{ik(x-x_j)} + B_j e^{-ik(x-x_j)}, \quad (2.129)$$

where (for now) $j = 1$ or 2 , and $(\hbar k)^2/2m = E$. Note that each of the wave pairs (129) has, in this notation, its own reference point x_j , because this is very convenient for the calculations which follow.

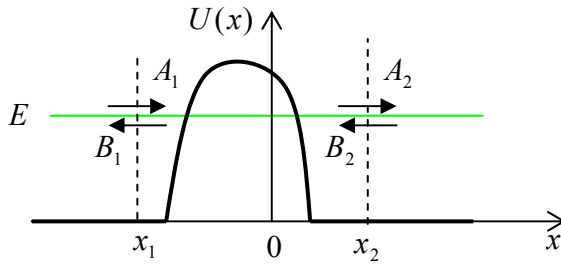


Fig. 2.13. A single 1D scatterer.

As we have already discussed, if the wave/particle is incident from the left, the linear Schrödinger equation within the scatterer range ($x_1 < x < x_2$), can provide only linear expressions of the transmitted (A_2) and reflected (B_1) wave amplitudes via the incident wave amplitude A_1 :

$$A_2 = S_{21}A_1, \quad B_1 = S_{11}A_1, \quad (2.130)$$

where S_{11} and S_{21} are certain (generally, complex) coefficients. In this case, $B_2 = 0$. Alternatively, if a wave, with amplitude B_2 , is incident from the right, it also may induce a transmitted wave (B_1) and reflected wave (A_2) with amplitudes

$$B_1 = S_{12}B_2, \quad A_2 = S_{22}B_2, \quad (2.131)$$

where coefficients S_{22} and S_{12} are generally different from S_{11} and S_{21} . Now we can use the linear superposition principle to argue that if waves A_1 and B_2 are simultaneously incident on the scatterer (say,

because wave B_2 has been partly reflected back by some other scatterer located at $x > x_2$), the resulting *scattered wave* amplitudes A_2 and B_1 are just the sums of their values for separate incident waves:

$$\begin{aligned} B_1 &= S_{11}A_1 + S_{12}B_2, \\ A_2 &= S_{21}A_1 + S_{22}B_2. \end{aligned} \quad (2.132)$$

These linear relations may be conveniently presented by the so-called scattering matrix (frequently called just “S-matrix”):

Scattering
matrix:
definition

$$\begin{pmatrix} B_1 \\ A_2 \end{pmatrix} = S \begin{pmatrix} A_1 \\ B_2 \end{pmatrix}, \quad S \equiv \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}. \quad (2.133)$$

Scattering matrices, duly generalized, are an important tool for the analysis of wave scattering in more than one dimensions; for 1D problems, however, another matrix is more convenient to present the same linear relations (132). Indeed, let us solve this system for A_2 and B_2 . The result is

Transfer
matrix:
definition

$$\begin{aligned} A_2 &= T_{11}A_1 + T_{12}B_1, \\ B_2 &= T_{21}A_1 + T_{22}B_1, \end{aligned} \quad \text{i.e.} \quad \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = T \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}, \quad (2.134)$$

where T is the *transfer matrix* with elements

$$T_{11} = S_{21} - \frac{S_{11}S_{22}}{S_{12}}, \quad T_{12} = \frac{S_{22}}{S_{12}}, \quad T_{21} = -\frac{S_{11}}{S_{21}}, \quad T_{22} = \frac{1}{S_{12}}. \quad (2.135)$$

One can wonder whether matrices S and T obey any universal properties that would be valid for an arbitrary (but time-independent) scatterer. Such universal equations may be readily found from the probability current conservation and the time-reversal symmetry of the Schrödinger equation. Let me leave finding these relations for reader’s exercise. The results show, in particular, that the scattering matrix may be rewritten in the following form:

$$S = e^{i\theta} \begin{pmatrix} re^{i\varphi} & t \\ t & -re^{-i\varphi} \end{pmatrix}, \quad (2.136a)$$

where 4 real parameters r , t , θ , and φ satisfy just one universal relation:

$$r^2 + t^2 = 1 \quad (2.136b)$$

(so that only 3 of the parameters are independent). As a result of this symmetry, T_{11} may be also presented in a simpler form, similar to T_{22} : $T_{11} = \exp\{i\theta\}/t = 1/S_{12}^* = 1/S_{21}^*$. The last form allows a ready expression of scatterer’s transparency via just one coefficient of the transfer matrix:

$$T \equiv \left| \frac{A_2}{A_1} \right|_{B_2=0}^2 = |S_{21}|^2 = |T_{11}|^{-2}. \quad (2.137)$$

In our current context, the most important property of 1D transfer matrices is that in order to find the total transfer matrix T of a system consisting of several (say, N) sequential arbitrary scatterers (Fig. 14), it is sufficient to multiply their matrices. Indeed, extending the definition (134) to other points x_j ($j = 1, 2, \dots, N+1$), we can write

$$\begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = T_1 \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}, \quad \begin{pmatrix} A_3 \\ B_3 \end{pmatrix} = T_2 \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = T_2 T_1 \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}, \quad (2.138)$$

etc. (where the matrix indices indicate the scatterers' order on axis x), so that

$$\begin{pmatrix} A_{N+1} \\ B_{N+1} \end{pmatrix} = T_N T_{N-1} \dots T_1 \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}. \quad (2.139)$$

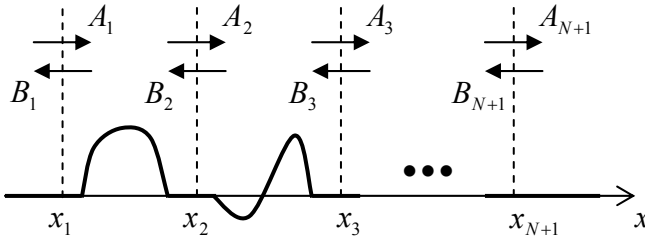


Fig. 2.14. A sequence of several 1D scatterers.

But we can also define the *total transfer matrix* similarly to Eq. (134), i.e. as

$$\begin{pmatrix} A_{N+1} \\ B_{N+1} \end{pmatrix} \equiv T \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}, \quad (2.140)$$

so that finally

$$T = T_N T_{N-1} \dots T_1. \quad (2.141)$$

Transfer
matrix of a
composite
scatterer

This formula is valid even if the flat-potential gaps between component scatterers vanish, so that it may be applied to a scatterer with an arbitrary profile $U(x)$, by fragmenting its length into small segments $\Delta x = x_{j+1} - x_j$, and treating each fragment as a rectangular barrier of height $(U_j)_{\text{ef}} = [U(x_{j+1}) - U(x_j)]/2$ - see Fig. 15. Since very efficient numerical algorithms are readily available for fast multiplication of matrices (especially as small as 2×2), this approach is broadly used in practice for the computation of transparency of tunnel barriers with complicated profiles $U(x)$. (This is much more efficient than the direct numerical solution of the Schrödinger equation.)

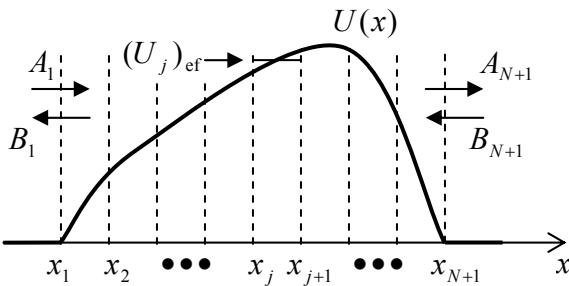


Fig. 2.15. The transfer matrix approach to a long tunnel barrier of an arbitrary profile.

In order to use this approach for several conceptually important systems, let us calculate the transfer matrices for a few elementary scatterers, starting from the delta-functional barrier located at $x = 0$. Taking $x_1 = x_2 = 0$, we can merely change the notation of wave amplitudes in Eq. (127) to get

$$S_{11} = \frac{-i\alpha}{1+i\alpha}, \quad S_{21} = \frac{1}{1+i\alpha}. \quad (2.142a)$$

An absolutely similar analysis of the wave incidence from the left yields

$$S_{22} = \frac{-i\alpha}{1+i\alpha}, \quad S_{12} = \frac{1}{1+i\alpha}, \quad (2.142b)$$

and using Eqs. (135), we get

$$T_\alpha = \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix}. \quad (2.143)$$

Transfer
matrix of a
short
scatterer

The next example may seem strange at the first glance: what if there is no scatterer at all between points x_1 and x_2 ? If points x_1 and x_2 coincide, the answer is indeed trivial and can be obtained, e.g., from Eq. (143) by taking $W = 0$, i.e. $\alpha = 0$:

$$T_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \equiv I \quad (2.144)$$

Identity
matrix

- the so-called *identity matrix*. However, we are free to choose the reference points $x_{1,2}$ participating in Eq. (129) as we wish. For example, what if $x_2 - x_1 = a$? Let us first take the forward-propagating wave alone: $B_2 = 0$ (and hence $B_1 = 0$); then

$$\psi_2 = \psi_1 = A_1 e^{ik(x-x_1)} = A_1 e^{ik(x_2-x_1)} e^{ik(x-x_2)}. \quad (2.145)$$

Comparison of this expression with the definition (129) for $j = 2$ shows that $A_2 = A_1 \exp\{ik(x_2 - x_1)\} = A_1 \exp\{ika\}$, i.e. $T_{11} = \exp\{ika\}$. Repeating the calculation for the back-propagating wave, we see that $T_{22} = \exp\{-ika\}$, and since this “no-potential” (space interval) provides no particle reflection, we finally get

$$T_a = \begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix}, \quad (2.146)$$

Transfer
matrix
of a space
interval

independently of the mutual position of points x_1 and x_2 . At $a = 0$, we naturally recover the special case (143).

Now let us use these results to analyze the *double-barrier system* shown in Fig. 16. We could of course calculate its properties as before, writing down explicit expressions for all 5 traveling waves shown by arrows in Fig. 16, and then using boundary conditions (124) and (125) at each of points $x_{1,2}$ to get a system of 4 linear equations, and then solving it for 4 amplitude ratios.

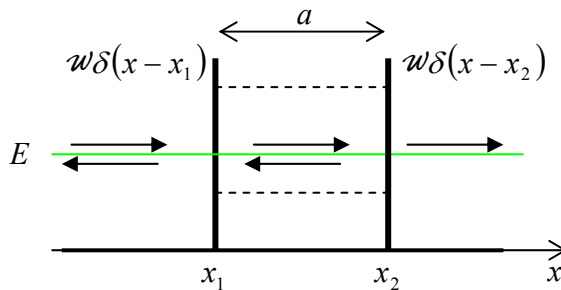


Fig. 2.16. Double-barrier system. Dashed lines show (schematically) the position of metastable energy levels.

However, the transfer matrix approach simplifies the calculations, because we may immediately use Eqs. (141), (143), and (146) to write

$$T = T_\alpha T_a T_\alpha = \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix} \begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix}. \quad (2.147)$$

Let me hope that the reader remembers the “row by column” rule of the multiplication of square matrices;³³ using it for two last matrices, we reduce Eq. (147) to

$$T = \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix} \begin{pmatrix} (1-i\alpha)e^{ika} & -i\alpha e^{ika} \\ i\alpha e^{-ika} & (1+i\alpha)e^{-ika} \end{pmatrix}. \quad (2.148)$$

Now there is no need to calculate all elements of the full product T , because, according to Eq. (137), for the calculation of barrier transparency T we need only one its element, T_{11} :

$$T = \frac{1}{|T_{11}|^2} = \frac{1}{|\alpha^2 e^{-ika} + (1-i\alpha)^2 e^{ika}|^2}. \quad (2.149)$$

Double
barrier
transparency

This result is similar to that following from Eq. (79) for $E > U_0$: the transparency is a π -periodic function of the product ka , reaching the maximum ($T = 1$) at some point of each period – see Fig. 17a.

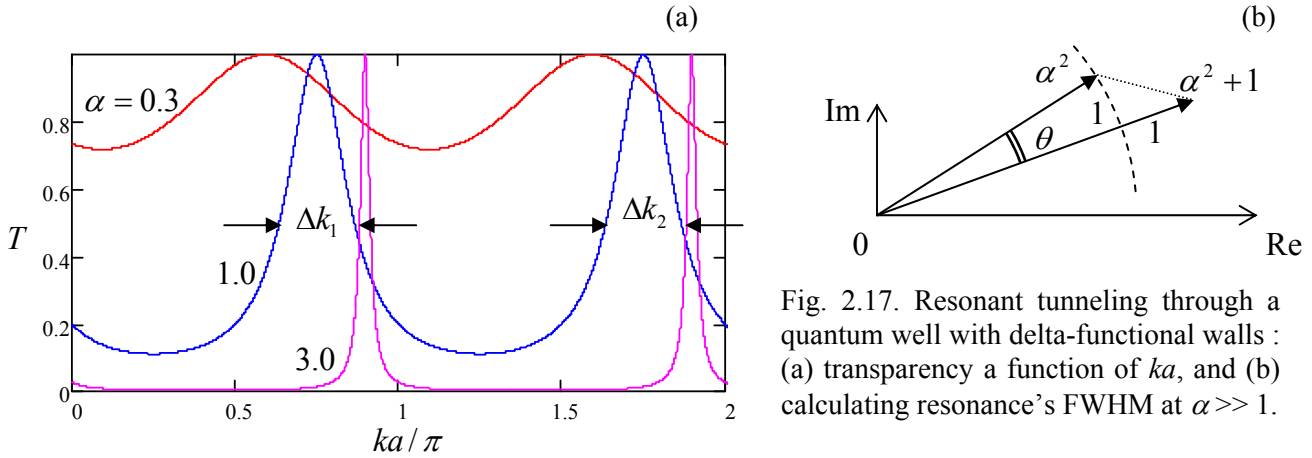


Fig. 2.17. Resonant tunneling through a quantum well with delta-functional walls : (a) transparency a function of ka , and (b) calculating resonance's FWHM at $\alpha \gg 1$.

However, the new result is different in that for $\alpha \gg 1$, the resonance peaks of transparency are very narrow, reaching their maxima at $ka \approx k_n a \equiv n\pi$, with $n = 1, 2, \dots$. Physics of this effect is immediately clear from the comparison of this result with our analysis of the simplest quantum well – see Fig. 1.7 and its discussion. At $k \approx k_n$, the incident wave, which undertakes multiple sequential reflections from the semi-transparent walls of the well, forms a nearly standing wave, which at $\alpha \gg 1$ virtually coincides with one of eigenfunctions of the well with infinite walls, with the standing wave amplitude much larger than that of the incident wave. As a result, the transmitted wave amplitude is

³³ In the analytical form: $(AB)_{jj'} = \sum_{j''=1}^N A_{jj''} B_{j''j'}$, where N is the matrix rank (in our current case, $N = 2$).

proportionately increased. This is the famous effect of *resonant tunneling*,³⁴ in mathematical description identical to the resonant transmission of light through an optical *Fabry-Perot resonator* formed by two parallel semi-transparent mirrors.³⁵

Probably, the most surprising feature of this system is the fact that its maximum transparency is *perfect* ($T_{\max} = 1$) even at $\alpha \rightarrow \infty$, i.e. in the case of a very *low* transparency of each of two component barriers.³⁶ Indeed, the denominator in Eq. (149) may be interpreted as the squared length of the difference between two vectors, one of length α^2 , and another of length $|(1 - i\alpha)^2| = 1 + \alpha^2$, with angle $\theta = 2ka + \text{const}$ between them. At the resonance, the vectors are aligned, and the difference is smallest (equal to 1) – see Fig. 17b, so that $T_{\max} = 1$.

We can use the same vector diagram to calculate the so-called FWHM, the common acronym for the *Full Width* [of the resonance curve at] *Half-Maximum*, i.e. the difference $\Delta k = k_+ - k_-$ between such two points on the opposite slopes of the same resonance, at which $T = T_{\max}/2$ – see arrows in Fig. 17a. Let the vectors in Fig. 17b be slightly misaligned, by an angle $\theta \sim 1/\alpha^2 \ll 1$, so that the length of the difference vector (of the order of $\alpha^2 \theta \sim 1$) is still much smaller than the length of each vector. In order to double its length squared, and hence reduce T by a factor of 2 in comparison with its maximum value 1, the arc, $\alpha^2 \theta$, between the vectors should also become equal ± 1 , i.e. $\alpha^2(2k_{\pm}a + \text{const}) = \pm 1$. Subtracting these two equations from each other, we finally get

$$\Delta k \equiv (k_+ - k_-) = \frac{1}{a\alpha^2} \ll k_{\pm}. \quad (2.150)$$

Now let us use the simple potential shown in Fig. 16 to discuss an issue of large conceptual importance. For that, consider what would happen if at some initial moment (say, $t = 0$) we have placed a 1D quantum particle inside the double-barrier well with $\alpha \gg 1$, and left it there alone, without any incident wave. To simplify the analysis, let us prepare the initial state so that it coincides with the ground state of the infinite-wall well – see Eq. (1.76):

$$\Psi(x, 0) = \psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin[k_1(x - x_1)] \quad \text{where } k_1 = \frac{\pi}{a}. \quad (2.151)$$

At $\alpha \rightarrow \infty$, this is an eigenstate of the system, and from our analysis in Sec. 1.5 we know its time evolution:

$$\Psi(x, t) = \psi_1(x) e^{-i\omega_1 t}, \quad \text{with } \omega_1 = \frac{E_1}{\hbar} = \frac{\hbar k_1^2}{2m} = \frac{\hbar \pi^2}{2ma^2}, \quad (2.152)$$

telling us that the particle remains in the well at all times with constant probability $W(t) = W(0) = 1$.³⁷

However, if parameter α is large but finite, the de Broglie wave should slowly “leak out” from the well, so that $W(t)$ would slowly decrease. Let us consider this effect approximately, assuming that

³⁴ In older literature, it is sometimes called the *Ramsauer* (or “Townsend”, or “Ramsauer-Townsend”) *effect*. However, it is currently more common to use that name(s) only for a similar 3D effect, especially at scattering of low-energy electrons on rare gas atoms – this is how it was first observed, independently, by C. Ramsauer and J. Townsend in the early 1920s.

³⁵ See also, e.g., EM Sec.7.9.

³⁶ The exact equality $T_{\max} = 1$ is correct only if both component barriers are exactly equal.

³⁷ Probability $W(t)$ should not be confused with the delta-functional barrier’s “area” $\mathcal{W}$, defined by Eq. (122).

the slow leakage, with a characteristic time $\tau \gg 1/\omega_1$, does not affect the instant wave distribution inside the well, besides the reduction of W .³⁸ Then we can generalize Eqs. (151), (152) as follows:

$$\Psi(x, t) = \left(\frac{2W}{a} \right)^{1/2} \sin[k_1(x - x_1)] e^{-i\omega_1 t}. \quad (2.153)$$

making the probability of finding the particle in the well equal to W . This solution may be presented as a sum of two traveling waves:

$$\Psi(x, t) = A e^{i(k_1 x - \omega_1 t)} + B e^{-i(k_1 x - \omega_1 t)}, \quad (2.154)$$

with equal magnitudes of their amplitudes and probability currents

$$|A| = |B| = \left(\frac{W}{2a} \right)^{1/2}, \quad I_A = \frac{\hbar}{m} |A|^2 k_1 = \frac{\hbar}{m} \frac{W}{2a} \frac{\pi}{a}, \quad I_B = -I_A. \quad (2.155)$$

But we already know from Eq. (128) that at $\alpha \gg 1$ the delta-functional wall transparency T approximately equals $1/\alpha^2$, so that the wave carrying current I_A , incident on the right wall from inside, induces an outgoing waves outside of the well (Fig. 18) with the following probability current:

$$I_R = \frac{1}{\alpha^2} I_A = \frac{1}{\alpha^2} \frac{\pi \hbar W}{2ma^2}. \quad (2.156a)$$

Absolutely similarly,

$$I_L = \frac{1}{\alpha^2} I_B = -I_R. \quad (2.156b)$$

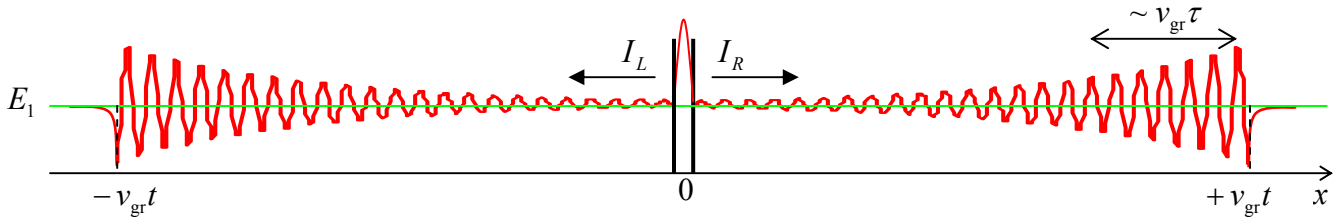


Fig. 2.18. Metastable state's decay in the simple model of a 1D potential well with low-transparent walls – schematically.

Now we may combine the 1D version (6) of the probability conservation law for well's interior,

$$\frac{dW}{dt} + I_R - I_L = 0, \quad (2.157)$$

with Eqs. (156) to write

$$\frac{dW}{dt} = -\frac{1}{\alpha^2} \frac{\pi \hbar}{ma^2} W. \quad (2.158)$$

³⁸ This almost evident assumption finds its formal justification in the perturbation theory to be discussed in Chapter 6.

This is just the standard differential equation,

Metastable
state's
decay law

$$\frac{dW}{dt} = -\frac{1}{\tau}W, \quad (2.159)$$

of the exponential decay, with solution $W(t) = W(0)\exp\{-t/\tau\}$, where constant τ , in our case equal to

$$\tau = \frac{ma^2}{\pi\hbar}\alpha^2, \quad (2.160)$$

is called the *metastable state's lifetime*. Using expression (2.34) for the de Broglie waves' group velocity, in our particular wave vector giving $v_{\text{gr}} = \hbar k_1/m = \pi\hbar/ma$, Eq. (159) may be rewritten as

Metastable
state's
lifetime

$$\tau = \frac{t_A}{T}, \quad (2.161)$$

where in our case the attempt time t_A is equal to a/v_{gr} , and $T = 1/\alpha^2$. Relation (161), that is valid for a large class of metastable systems,³⁹ may be interpreted in the following semi-classical way. The confined particle travels back and forth between the confining walls, with time intervals t_A between the moments of incidence, each time making an attempt to leak through the wall, with a success probability of T , so the reduction of W per each incidence is $\Delta W = -WT$, immediately leading to Eq. (161).

Another important look at Eq. (160) may be taken by returning to the resonant tunneling problem and expressing the resonance width (150) in terms of incident particle's energy:

$$\Delta E = \Delta \left(\frac{\hbar^2 k^2}{2m} \right) \approx \frac{\hbar^2 k_1}{m} \Delta k = \frac{\hbar^2 k_1}{m} \frac{1}{a\alpha^2} = \frac{\pi\hbar^2}{ma^2\alpha^2}. \quad (2.162)$$

Comparing Eqs. (160) and (162), we get a remarkably simple formula

Energy-time
uncertainty
relation

$$\Delta E \cdot \tau = \hbar. \quad (2.163)$$

This so-called *energy-time uncertainty relation* is certainly *more* general than our simple model; for example, it is valid for the lifetime and resonance tunneling width of any metastable state. This seems very natural, since because of the energy identification with frequency, $E = \hbar\omega$, typical for quantum mechanics, Eq. (163) may be rewritten as $\Delta\omega \cdot \tau = 1$ and seems to follow directly from the Fourier transform in time, just as the Heisenberg's uncertainty relation (1.35) follows from the Fourier transform in space. In some cases, these two relations are indeed interchangeable; for example, Eq. (24) for the Gaussian wave packet width may be rewritten as $\delta E \cdot \Delta t = \hbar$, where $\delta E = \hbar(d\omega/dk)\delta k = \hbar v_{\text{gr}}\delta k$ is the r.m.s. spread of energies of monochromatic components of the packet, while $\Delta t \equiv \delta x/v_{\text{gr}}$ is the time scale of the packet passage through a fixed observation point x .

However, Eq. (163) it is much *less* general than Heisenberg's uncertainty relation (1.35). Indeed, in nonrelativistic quantum mechanics, Cartesian coordinates (say, x) of a particle, components of its momentum (say, p_x), and energy E are regular observables, presented by operators. In contrast, time is treated as a *c*-number argument, and is *not* presented by an operator, so that Eq. (163) cannot be derived

³⁹ Essentially the only requirement is to have the attempt time Δt_A to be much longer than the effective time (*instanton time*, see Sec. 5.3 below) of tunneling through the barrier. In the delta-functional approximation for the barrier, the latter time vanishes, so that this requirement is always fulfilled.

in such general assumptions as Eq. (1.35). Thus the time-energy uncertainty relation should be applied with great caution. Unfortunately, not everybody is so careful. One can find, for example, wrong claims that due to this relation, the energy dissipated by any system performing an elementary (single-bit) calculation during time interval Δt has to be larger than $\hbar/\Delta t$.⁴⁰ Another incorrect statement is that the energy of a system cannot be measured, during time Δt , with an accuracy better than $\hbar/\Delta t$.⁴¹

Now let us use our simple model of metastable state's decay for a preliminary discussion of one aspect of quantum measurements. Figure 18 shows (schematically) one of the traveling wave packets emitted by the quantum well after its initial state (152) had been prepared at $t = 0$. (A similar packet is emitted to the left.) At $t \gg \tau$, the well becomes essentially empty ($W \ll 1$), and the whole probability distribution is localized in two clearly separated wave packets of equal amplitudes, moving from away with speed v_{gr} , each “carrying the particle away” with a probability of 50%. Now assume an experiment has detected the particle on the left side of the well. Though the formalisms suitable for a quantitative analysis of the detection process will not be discussed until Sec. 7.7, due to the wide separation of the packets, we may safely assume that the detection may be done without any actual physical effect on the counterpart wave packet.⁴² But if we know that the particle has been found on the left, there is no chance to find it on the right.

If we attributed the wavefunction to all stages of this particular experiment, this situation might be rather confusing. Indeed, this would mean that the wavefunction within the right packet should instantly turn into zero - the so-called *wave packet reduction* - a process that could not be described by either Schrödinger equation or any other law of physics. However, if (as was already discussed in Sec. 1.3) we attribute the wavefunction to a statistical ensemble of similar experiments, there is no paradox here at all. While the two-packet picture we have calculated (Fig. 18) describes the full initial ensemble (regardless of the particle detection results), the “reduced packet” picture (with no wave packet on the right of the well) describes only a sub-ensemble of experiments with the particle detected on the left side. As was discussed on completely classical examples in Sec. 1.3, for such sub-ensemble the probability distribution, and hence the wavefunction, may be dramatically different.

2.6. Coupled quantum wells

Let us now move on to tunneling through a more complex potential profile shown in Fig. 19: a sequence of $(N - 1)$ similar quantum wells separated by N similar delta-functional tunnel barriers. According to Eq. (141), its transfer matrix is the following product

$$T = \underbrace{T_\alpha T_a T_\alpha \dots T_a T_\alpha}_{(N-1)+N \text{ terms}}, \quad (2.164)$$

with the component matrices given by Eqs. (143) and (146), and the barrier height parameter α defined by the last of Eqs. (127).

⁴⁰ Here I dare to refer the reader to my own old work K. Likharev, *Int. J. Theor. Phys.* **21**, 311 (1982) that presented a constructive proof that at *reversible computation* (introduced in 1973 by C. Bennett) the energy dissipation may be lower than this apparent “quantum limit”.

⁴¹ See, e.g., a detailed discussion of this issue in the monograph by V. Braginsky and F. Khalili, *Quantum Measurement*, Cambridge U. Press, 1992.

⁴² This argument is especially convincing if the particle detection time is much shorter than the time $t_c = 2v_{gr}t/c$, where c is the speed of light in vacuum, i.e. the maximum velocity of any information transfer (“signaling”).

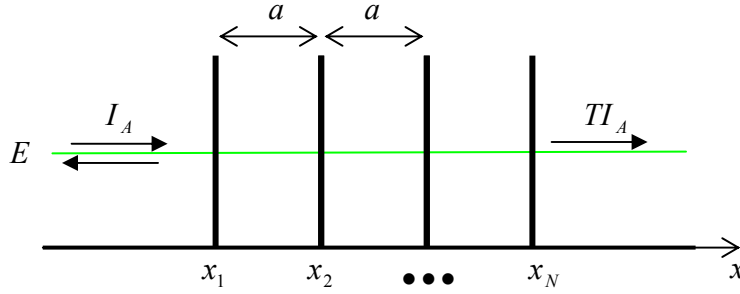


Fig. 2.19. Resonant tunneling through a system of N similar, equidistant barriers, i.e. $(N - 1)$ similar quantum wells.

Remarkably, this multiplication may be carried out analytically,⁴³ giving

$$T \equiv |T_{11}|^{-2} = \left[(\cos Nqa)^2 + \left(\frac{\sin ka - \alpha \cos ka}{\sin qa} \sin Nqa \right)^2 \right]^{-1}, \quad (2.165)$$

where q is a new parameter, with the wave number dimensionality, defined by the following relation:

$$\cos qa \equiv \cos ka + \alpha \sin ka. \quad (2.166)$$

For $N = 1$, Eqs. (165) and (166) immediately yield our old result (128), while for $N = 2$ they may be reduced to Eq. (149) – see Fig. 17a. Figure 20 shows its predictions for two larger numbers N , and several values of parameter α .

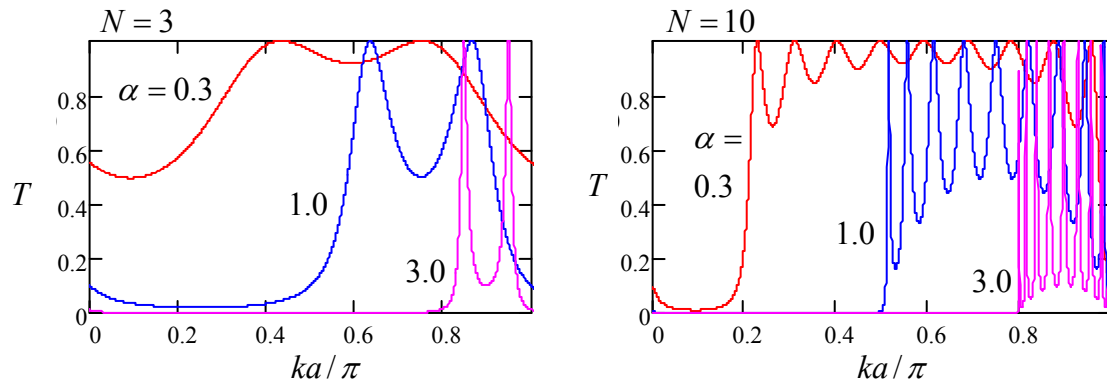


Fig. 2.20. Transparency of the system shown in Fig. 19 as a function of product ka . Since the function $T(ka)$ is π -periodic (just like for $N = 2$, see Fig. 17a), only one period is shown.

Let us start discussion of the plots from case $N = 3$, i.e. two coupled quantum wells. The comparison of Fig. 20a and Fig. 17a shows that the transmission patterns, and their dependence on parameter α , are very similar, besides that in the coupled wells each resonant tunneling peak splits into two, with the ka -difference between them scaling as $1/\alpha$. In order to comprehend the physics of this important result, let us analyze an auxiliary system shown in Fig. 21: two similar quantum wells

⁴³ This formula will be easier to prove after we have discussed properties of Pauli matrices in Chapter 4.

confined by infinitely high potential walls at $x = \pm a$, and coupled via a transparent, short tunnel barrier at $x = 0$.

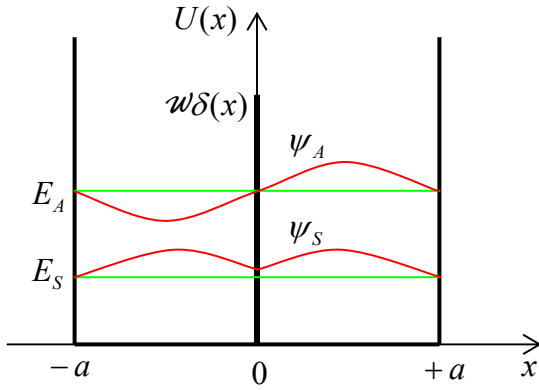


Fig. 2.21. Two lowest eigenfunctions and eigenenergies of a system of two coupled quantum wells – schematically.

The barrier may be again, for calculation simplicity, approximated by a delta-function:

$$U(x) = \begin{cases} +\infty, & \text{for } |x| > a, \\ w\delta(x), & \text{for } |x| < a. \end{cases} \quad (2.167)$$

We already know that the standing-wave eigenfunctions ψ_n of the Schrödinger equation in regions with $U(x) = 0$, in our current case, segments $-a < x < 0$ and $0 < x < +a$, may be always presented as linear superpositions of $\sin kx$ and $\cos kx$. In order to immediately satisfy the boundary conditions $\psi = 0$ at $x = \pm a$, we can take these solutions in the form

$$\psi_n(x) = \begin{cases} C_- \sin k(x+a), & \text{for } -a < x < 0, \\ C_+ \sin k(x-a), & \text{for } 0 < x < +a. \end{cases} \quad (2.168)$$

What remains is to satisfy the boundary conditions at $x = 0$. Plugging Eq. (167) into Eqs. (124) and (125), we get the following system of two linear equations:

$$k(C_+ - C_-) \cos ka = \frac{2m\omega}{\hbar^2} C_- \sin ka, \quad (2.169)$$

$$C_- \sin ka = -C_+ \sin ka. \quad (2.170)$$

The system has two types of solutions, with the two lowest-energy eigenfunctions sketched in Fig. 21:

(i) *Antisymmetric solutions* (which will be marked with index A),

$$(C_+)_A = (C_-)_A, \quad \text{i.e. } \psi_A = C_A \sin k_A x, \quad (2.171)$$

with eigenvalues independent of W ,

$$\sin k_A a = 0, \quad \text{i.e. } k_A a = k n a \equiv \pi n, \quad n = 1, 2, \dots \quad (2.172)$$

Notice that these values of k , and hence eigenenergies of these antisymmetric states,

$$E_A = \frac{\hbar^2 k_A^2}{2m} = \frac{\pi^2 n^2}{2ma^2}, \quad (2.173)$$

coincide with those of the simple quantum well of width a – see Fig. 1.7 and its discussion.

(ii) *Symmetric solutions* (index S):

$$(C_+)_S = -(C_-)_S, \quad \text{i.e. } \psi_S = C_S |\sin k_S(x - a)|, \quad (2.174)$$

with Eq. (169) giving the following *characteristic equation* for constant k_S :

$$\tan k_S a = -\frac{1}{\alpha}. \quad (2.175)$$

Figure 22 shows the graphic solution of this equation for three values of parameter α , i.e. for various quantum well coupling strength. For each solution, $k_S a$ is confined within interval

$$\pi m < k_S a < \pi m - \frac{\pi}{2}, \quad (2.176)$$

so that the antisymmetric and symmetric states alternate on the scale of k (and hence of the energy), with the difference $k_A - k_S$, for each pair of adjacent states, smaller than $\pi/2a$ for any value of α . The physics of the splitting between eigenenergies corresponding to the symmetric and antisymmetric states is very simple: it is the change of kinetic energy of the particle due to different confinement types – see Fig. 21. In each antisymmetric mode, $\psi_n(0) = \psi_n(\pm a) = 0$, i.e. the wavefunction is essentially confined within a segment of length a ; as a result, its energy (173) does not depend on the barrier height. On the contrary, in the symmetric mode, that does engage the potential barrier, the wavefunction effectively spreads into the counterpart well. As a result, it changes slower, and hence its kinetic energy is also lower than that of the adjacent antisymmetric mode.

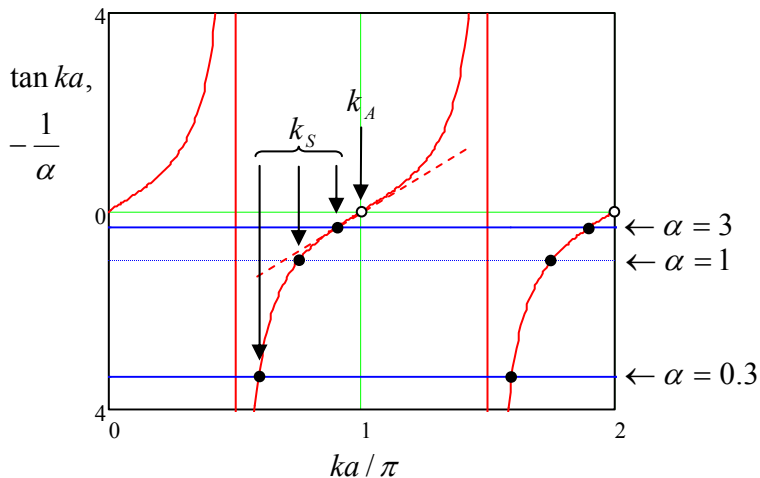


Fig. 2.22. Graphical solution of the characteristic equation (175) for the eigenvalue of ka in the symmetric mode, for 3 values of parameter α , considering it independent of ka . The dashed line shows approximation (178).

By the way, this problem may serve as a toy model of the strongest (and most important) type of atom cohesion - the *covalent* (or “chemical”) bonding in molecules, liquids, and solids. The classical example of such bonding is that of hydrogen atoms in a H_2 molecule.⁴⁴ Each of two electrons of this system⁴⁵ reduces its kinetic energy very substantially by spreading its wavefunction around both nuclei

⁴⁴ Historically, the development of the fully quantum theory of H_2 bonding by W. Heitler and F. London in 1927 was the breakthrough decisive for the acceptance of then-emerging quantum mechanics by chemists.

⁴⁵ Due to the opposite spins, the Pauli principle allows them to be in the same orbital ground state – see Chapter 8.

protons, rather than being confined near one of them - as it had to be in a single atom. As a result, the bonding is very strong: in chemical units, 429 kJ/mol, i.e. 18.6 eV per molecule.⁴⁶ Somewhat counter-intuitive, this energy is substantially larger than the strongest classical (*ionic*) bonding due to electron transfer between atoms, leading to the Coulomb attraction of the resulting ions. (For example, the atomic cohesion in the NaCl molecule is just 3.28 eV.)

In the limit $\alpha \rightarrow 0$ (no partition between the wells), $k_S a \rightarrow \pi(n - 1/2)$, i.e. the eigenstates approach the shape and energy of symmetric states of a quantum well of width $2a$. In the opposite limit $\alpha \gg 1$, $k_S a \rightarrow \pi n$, and in the vicinity of each such point we may approximate $\tan k_S a$ with $(k_S a - \pi n)$ – see the dashed line in Fig. 22. As a result, the characteristic equation (175) is reduced to

$$k_S a \approx \pi n - \frac{1}{\alpha}, \quad (2.177)$$

so that the splitting between the wave numbers and eigenenergies of the adjacent symmetric and antisymmetric states is small:

$$k_A - k_S \approx \frac{1}{\alpha a} \ll k_n, \quad 2\delta_n \equiv E_A - E_S \approx \frac{dE}{dk}(k_A - k_S) = \frac{\pi \hbar^2}{ma} \frac{1}{\alpha a} = \frac{2E_A}{\pi \alpha}. \quad (2.178)$$

(By construction, this result is valid only if $\alpha \gg 1$, i.e. $\delta_n \ll E_A \approx E_S$.)

Let us analyze properties of the system in this limit in much more detail - first, because the results will help us to develop the important *tight binding approximation* in the band theory, and second, because the weakly coupled quantum wells will be our first example of very important *two-level* (or “spin-1/2-like”) *systems*. Let us focus on one couple of symmetric and antisymmetric states, corresponding to virtually the same E_n . According to Eqs. (171) and (174), in the limit $\alpha \rightarrow \infty$, system's eigenfunctions may be approximately represented as follows:

$$\psi_S(x) \approx \frac{1}{\sqrt{2}} [\psi_R(x) + \psi_L(x)], \quad \psi_A(x) \approx \frac{1}{\sqrt{2}} [\psi_R(x) - \psi_L(x)], \quad (2.179)$$

where $\psi_{R,L}$ are the normalized ground states of the completely insulated wells:

$$\psi_R(x) = \begin{cases} 0, & \text{for } -a < x < 0, \\ (2/a)^{1/2} \sin k_n x, & \text{for } 0 < x < +a, \end{cases} \quad \psi_L(x) = \begin{cases} -(2/a)^{1/2} \sin k_n x, & \text{for } -a < x < 0, \\ 0, & \text{for } 0 < x < +a. \end{cases} \quad (2.180)$$

Let us perform the following conceptually important thought experiment: place the particle, at $t = 0$, into one of the localized states, say $\psi_R(x)$, and leave the system alone to evolve. Solving Eqs (180) for ψ_R , we may present the initial state as a linear superposition of eigenfunctions:

$$\Psi(x,0) = \psi_R(x) \approx \frac{1}{\sqrt{2}} [\psi_S(x) + \psi_A(x)]. \quad (2.181)$$

Now, according to the general solution (1.67) of the time-dependent Schrödinger equation, time dynamics may be obtained by just multiplying each eigenfunction by the corresponding factor (1.61):

⁴⁶ Unit reminder: 1 kJ/mol $\approx$ 0.0434 eV.

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \left[\psi_S(x) \exp\left\{-i \frac{E_S}{\hbar} t\right\} + \psi_A(x) \exp\left\{-i \frac{E_A}{\hbar} t\right\} \right]. \quad (2.182)$$

Now, introducing the following natural notation,

$$E_n \equiv \frac{E_A + E_S}{2}, \quad \delta_n \equiv \frac{E_A - E_S}{2}. \quad (2.183)$$

And using Eqs. (179), this expression may be rewritten as

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2}} \left[\psi_S(x) \exp\left\{i \frac{\delta_n}{\hbar} t\right\} + \psi_A(x) \exp\left\{-i \frac{\delta_n}{\hbar} t\right\} \right] \exp\left\{-i \frac{E_n}{\hbar} t\right\} \\ &= \left[\psi_R(x) \cos \frac{\delta_n}{\hbar} t + i \psi_L(x) \sin \frac{\delta_n}{\hbar} t \right] \exp\left\{-i \frac{E_n}{\hbar} t\right\}. \end{aligned} \quad (2.184)$$

This result implies, in particular, that the probabilities W_R and W_L to find the particle, correspondingly, in the right and left wells change with time as

Quantum
oscillations
in two
coupled
wells

$$W_R = \cos^2 \frac{\delta_n}{\hbar} t, \quad W_L = \sin^2 \frac{\delta_n}{\hbar} t, \quad (2.185)$$

mercifully leaving the total probability constant $W_R + W_L = 1$. (If our calculation had not passed this sanity check, we would be in a big trouble.)

This is the famous effect of periodic *quantum oscillations*, with frequency $\omega_n = 2\delta_n/\hbar = (E_A - E_S)/\hbar$, of the particle between two similar quantum wells, due to their coupling through via tunneling through the tunnel barrier. The physics of this effect is straightforward: just as in the single well problem discussed in Sec. 5, the particle initially placed into a certain quantum well tries to escape from it via tunneling through the semi-transparent wall. However, in our current situation (Fig. 21) the particle can only escape into the adjacent well. After the tunneling into that second well, the tries to escape from it, and hence comes back, etc. - just as a classical 1D oscillator, initially deflected from its equilibrium position.

Maybe the most surprising feature of this effect is its relatively high frequency: according to Eq. (178), the time period of the quantum oscillations,

$$\Delta t_n \equiv \frac{2\pi}{\omega_n} = \frac{2\pi\hbar}{(E_A - E_S)} \approx \frac{2\pi}{n} \frac{ma^2}{\pi\hbar} \alpha, \quad \text{for } \alpha \gg 1, \quad (2.186)$$

is a factor of $\alpha/2\pi \gg 1$ *shorter* than the lifetime τ (160) of the metastable state of the particle in a similar but single quantum well limited by delta-functional walls with similar parameter α . This is a very counterintuitive result indeed: the speed of particle tunneling into a similar adjacent well is much higher than that, through a similar barrier, to the free space!

To see whether this result is an artifact of the delta-functional model of the tunnel barrier, let us calculate splitting $2\delta_n$ for system of two similar, symmetric, soft quantum wells formed by a smooth potential profile $U(x) = U(-x)$ – see Fig. 23.

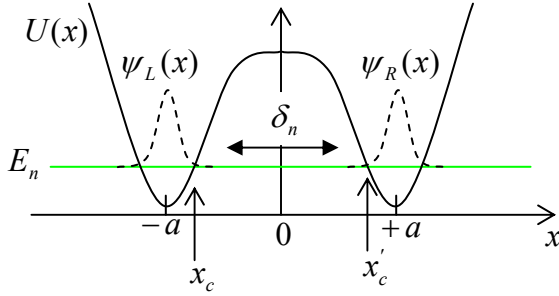


Fig. 2.23. Weak coupling between two similar, soft quantum wells.

If the barrier transparency is low, the quasi-localized wavefunctions $\psi_R(x)$ and $\psi_L(x) = \psi_R(-x)$ and their eigenenergies may be found approximately by solving the Schrödinger equations in one of the wells, neglecting tunneling through the barrier, but finding δ_n requires a little bit more care. Let us write the stationary Schrödinger equations for the symmetric and antisymmetric solutions in the form

$$[E_A - U(x)]\psi_A = -\frac{\hbar^2}{2m} \frac{d^2\psi_A}{dx^2}, \quad [E_S - U(x)]\psi_S = -\frac{\hbar^2}{2m} \frac{d^2\psi_S}{dx^2}, \quad (2.187)$$

then multiply the former equation by ψ_S , the latter one by ψ_A , subtract them from each other, and integrate the result from 0 to ∞ :

$$(E_A - E_S) \int_0^\infty \psi_S \psi_A dx = \frac{\hbar^2}{2m} \int_0^\infty \left[\frac{d^2\psi_S}{dx^2} \psi_A - \frac{d^2\psi_A}{dx^2} \psi_S \right] dx. \quad (2.188)$$

If $U(x)$, and hence $d^2\psi_{A,S}/dx^2$, are finite for all x ,⁴⁷ we may integrate the right-hand side by parts to get

$$(E_A - E_S) \int_0^\infty \psi_S \psi_A dx = \frac{\hbar^2}{2m} \left[\frac{d\psi_S}{dx} \psi_A - \frac{d\psi_A}{dx} \psi_S \right]_0^\infty. \quad (2.189)$$

So far, this is an exact equation. For weakly coupled wells, we can do more. In this case, the left hand side may be approximated as $(E_A - E_S)/2 \equiv \delta_n$, because the integral is dominated by the vicinity of point a , where the second terms in each of Eqs. (179) are negligible, and the integral is equal to $1/2$, due to the proper normalization of function $\psi_R(x)$. In the right-hand side, the substitution at $x = \infty$ vanishes (due to the wavefunction decay in the classically forbidden region), and so does the first term at $x = 0$, because for the antisymmetric solution $\psi_A(0) = 0$. As a result, we get

$$\delta_n = \frac{\hbar^2}{2m} \psi_S(0) \frac{d\psi_A}{dx}(0) = \frac{\hbar^2}{m} \psi_R(0) \frac{d\psi_R}{dx}(0) = \frac{\hbar^2}{m} \psi_L(0) \frac{d\psi_R}{dx}(0) = -\frac{\hbar^2}{m} \psi_L(0) \frac{d\psi_L}{dx}(0). \quad (2.190)$$

It is straightforward to show that within the limits of the WKB approximation validity, Eq. (190) may be reduced to

$$\delta_n = \frac{\hbar}{t_A} \exp \left\{ - \int_{x_c}^{x'_c} \kappa(x') dx' \right\}, \quad (2.191)$$

WKB
result
for
coupling
energy

⁴⁷ Since it is not true for potential (167), one should not be surprised that the resulting Eq. (189) is invalid for our initial problem, giving δ_n twice larger than the correct expression (178).

where t_A is the time period of classical motion of the particle inside one of the wells, function $\kappa(x)$ is defined by Eq. (97), and x_c and x_c' are the classical turning points limiting the potential barrier at the level E_n of particle's energy – see Fig. 23. Comparing this result with Eq. (117), we can notice that again, just as in the case of the delta-functional barriers, the transmission coefficient T of a tunnel barrier (and hence the reciprocal lifetime of a metastable state in a potential well separated by such a barrier from a *continuum*) scales as the square of the WKB exponent participating in Eq. (191), so that the period of quantum oscillations between the well is much smaller than the lifetime. We will return to the discussion of this result, in a more general form, in Chapter 5.

Returning for a second to Fig. 20a, we may now readily interpret the results for tunneling through the double quantum well: each pair of resonance peaks of transparency corresponds to the alignment of incident particle's energy with the pair of energy levels E_A , E_S of the symmetric and antisymmetric states of the system.

2.7. 1D band theory

Let us now return to Eqs. (165) and (166) describing the resonant tunneling, and discuss their predictions for larger N – see, for example, Fig. 20b. We see that the increase of N results in the increase of the number of resonant peaks per period to $(N - 1)$, and at $N \rightarrow \infty$ the peaks merge into the so-called *allowed energy bands* (frequently called just the “energy bands”) of relatively high transparency, separated from similar bands in the adjacent periods of function $T(ka)$ by *energy gaps*⁴⁸ where $T \rightarrow 0$. Notice the following important features of the pattern:

- (i) at $N \rightarrow \infty$, the band/gap edges become sharp for any α , and tend to fixed positions (determined by α but independent of N);
- (ii) the larger interwell coupling ($\alpha \rightarrow 0$), the broader the allowed energy bands and narrower the gaps between them.

Our discussion of resonant tunneling in the previous section gives us an evident clue for a semi-quantitative interpretation of this pattern: if $(N - 1)$ quantum wells are weakly coupled by tunneling through the tunnel barriers separating them, system's energy spectrum consists of groups $(N - 1)$ energy levels. Each level corresponds to an eigenfunction that is the set of similar local functions in each well, but with certain phase shifts $\Delta\varphi$ between them. It is natural to expect that, just as for 2 coupled wells ($N - 1 = 2$), that at the upper level, $\Delta\varphi = \pi$ (thus providing the highest confinement), with $ka \rightarrow \pi n$ at $\alpha \rightarrow \infty$, while at the lowest level all $\Delta\varphi = 0$, providing the most loose confinement.⁴⁹ However, what about $\Delta\varphi$ for other levels?

Answers to all these questions are easy to get in the most important limit $N \rightarrow \infty$, i.e. for *periodic structures* - which are, in particular, good 1D approximations for solid state crystals, whose samples may feature more than 10^{10} similar atoms or molecules in each direction of the crystal lattice. It is almost self-evident that at $N \rightarrow \infty$, due to the translational invariance of $U(x)$,

$$U(x + a) = U(x), \quad (2.192)$$

⁴⁸ In solid state (especially semiconductor) physics and electronics, term *bandgaps* is more common.

⁴⁹ This expectation is implicitly confirmed by Fig. 20: at $\alpha \gg 1$, the highest resonance peak in each group tends to $ka = \pi n$, and the lowest peak also tend to a position independent of N (though dependent on α).

the phase shift $\Delta\varphi$ between local wavefunctions in all adjacent quantum wells should be the same for each period of the system, i.e.

$$\psi(x+a) = \psi(x)e^{i\Delta\varphi} \quad (2.193a)$$

for all x . (A reasonably fair classical image of $\Delta\varphi$ is the geometric angle between similar objects - e.g., similar paper clips - attached at equal distances to a long, uniform rubber band. If the band's ends are twisted, the twist is equally distributed between the structure's periods, representing the constancy of $\Delta\varphi$.⁵⁰)

Equation (193a) is the (1D version of the) much-celebrated *Bloch theorem*.⁵¹ Mathematical rigor aside,⁵² it is a virtually evident fact, because the particle's density $w(x) = \psi^*(x)\psi(x)$, that has to be periodic in this a -periodic system, may be so only $\Delta\varphi$ is constant. For what follows, it is more convenient to present the real number $\Delta\varphi$ in the form qa (there is no loss of generality here, because parameter q may depend on a as well as other parameters of the system), so that the Bloch theorem takes the form

$$\psi(x+a) = \psi(x)e^{iqa} \quad (2.193b)$$

1D Bloch theorem

The physical sense of parameter q will be discussed in detail below; for now just note that according to Eq. (193b), an addition of $(2\pi/a)$ to it yields the same wavefunction; hence all observables have to be $(2\pi/a)$ -periodic functions of q .⁵³

Now let us use the Bloch theorem to find eigenfunctions and eigenenergies for a particular, and probably the simplest periodic function $U(x)$: an infinite set of similar quantum wells separated by delta-functional tunnel barriers (Fig. 24).

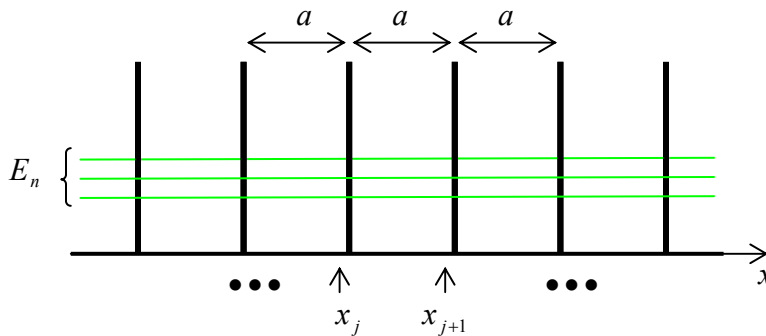


Fig. 2.24. The simplest periodic potential: an infinite set of similar, equidistant, delta-functional tunnel barriers.

⁵⁰ I am ashamed to confess that, due to the lack of time, this was virtually the only “lecture demonstration” in my QM courses.

⁵¹ Named after F. Bloch who applied this concept to wave mechanics in 1929, i.e. very soon after its formulation. Admittedly, in mathematics, an equivalent statement, usually called the *Floquet theorem*, has been known since at least 1883.

⁵² I will address this rigor in two steps. Later in this section, we will see that the function obeying Eq. (193) is indeed a solution of the Schrödinger equation. However, to save time/space, it will be better for us to postpone the proof that *any* eigenfunction of the equation, with periodic boundary conditions, obeys the Bloch theorem, until Chapter 4. As a partial reward for the delay, that proof will be valid for an arbitrary spatial dimensionality.

⁵³ Product $\hbar q$, which has the dimensionality of momentum, is called either the *quasi-momentum* or (especially in the solid state physics) the “crystal momentum” of the particle.

To start, consider two points separated by distance a : one of them, x_j , just left of position of one of the barriers, and another one, x_{j+1} , just left of the following barrier. Eigenfunctions in each of the points may be presented as linear superpositions of two simple waves $\exp\{\pm ikx\}$, and amplitudes of their components should be related by a 2×2 transfer matrix T of the potential fragment separating them. According to Eq. (141), this matrix may be found as the product of the matrix (146) of one interval a and the matrix (143) of one barrier:

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = T_a T_\alpha \begin{pmatrix} A_j \\ B_j \end{pmatrix} = \begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix} \begin{pmatrix} A_j \\ B_j \end{pmatrix}. \quad (2.194)$$

However, according to the Bloch theorem (193b), the component amplitudes should be also related as

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = e^{iqa} \begin{pmatrix} A_j \\ B_j \end{pmatrix} = \begin{pmatrix} e^{iqa} & 0 \\ 0 & e^{iqa} \end{pmatrix} \begin{pmatrix} A_j \\ B_j \end{pmatrix}. \quad (2.195)$$

The condition of self-consistency of these two equations leads to the following characteristic equation:

$$\left[\begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix} - \begin{pmatrix} e^{iqa} & 0 \\ 0 & e^{iqa} \end{pmatrix} \right] = 0. \quad (2.196)$$

In Sec. 5, we have already calculated the matrix product participating in this equation – see Eq. (148). Using it, we see that Eq. (196) is reduced to the same simple Eq. (166) that has already jumped at us from the solution of the different (resonant tunneling) problem. Let us explore that simple result in detail. First of all, the right hand part of Eq. (166) is a sinusoidal function of ka , with amplitude $(1 + \alpha^2)^{1/2}$ – see Fig. 25, while its left hand part is a sinusoidal function of qa with amplitude 1.

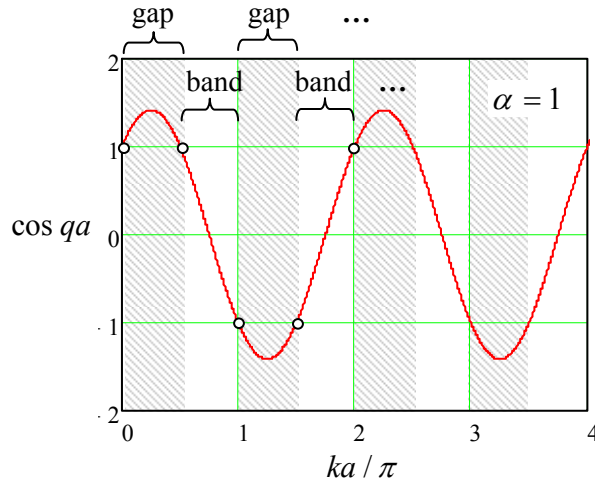


Fig. 2.25. Graphical solution of the characteristic equation (166) for a fixed value of parameter α . The ranges of ka that yield with $|\cos qa| < 1$, correspond to the allowed energy bands, while those with $|\cos qa| > 1$, to gaps between them.

As a result, within each period $\Delta(ka) = 2\pi$, the characteristic equation does not have a real solution for q inside two intervals of ka - and hence inside two intervals of energy $E = \hbar^2 k^2 / 2m$. (These intervals are exactly the energy gaps mentioned above, while the complementary intervals of ka and E , where a real q exists, are the allowed energy bands.) In contrast, parameter q can take *any* real values, so it is more convenient to plot the eigenenergy $E = \hbar^2 k^2 / 2m$ as the function of q (or, even more

conveniently, qa) rather than ka .⁵⁴ While doing that, we need to recall that parameter α , defined by the last of Eqs. (127), depends on wave vector k as well, so that if we vary q (and hence k), it is better to characterize the structure by a different, k -independent dimensionless parameter, for example

$$\beta \equiv (ka)\alpha = \frac{ma\omega}{\hbar^2}, \quad (2.197)$$

so that Eq. (166) becomes

$$\cos qa \equiv \cos ka + \beta \frac{\sin ka}{ka}. \quad (2.198)$$

Characteristic
equation
for system
in Fig. 24

Figure 26 shows the plots of E and k , following from Eq. (198), for a particular, moderate value of parameter β . The band structure of the energy spectrum is apparent. Another evident feature is the 2π -periodicity of the pattern, that we have already predicted from the general Bloch theorem arguments. (Due to this periodicity, the complete band/gap pattern may be studied on just one interval $-\pi \leq qa \leq +\pi$, called the *1st Brillouin zone* – the so-called *reduced zone picture*. For some applications, however, it is more convenient to use the *extended zone picture* with $-\infty \leq qa \leq +\infty$ – see, e.g., the next section.)

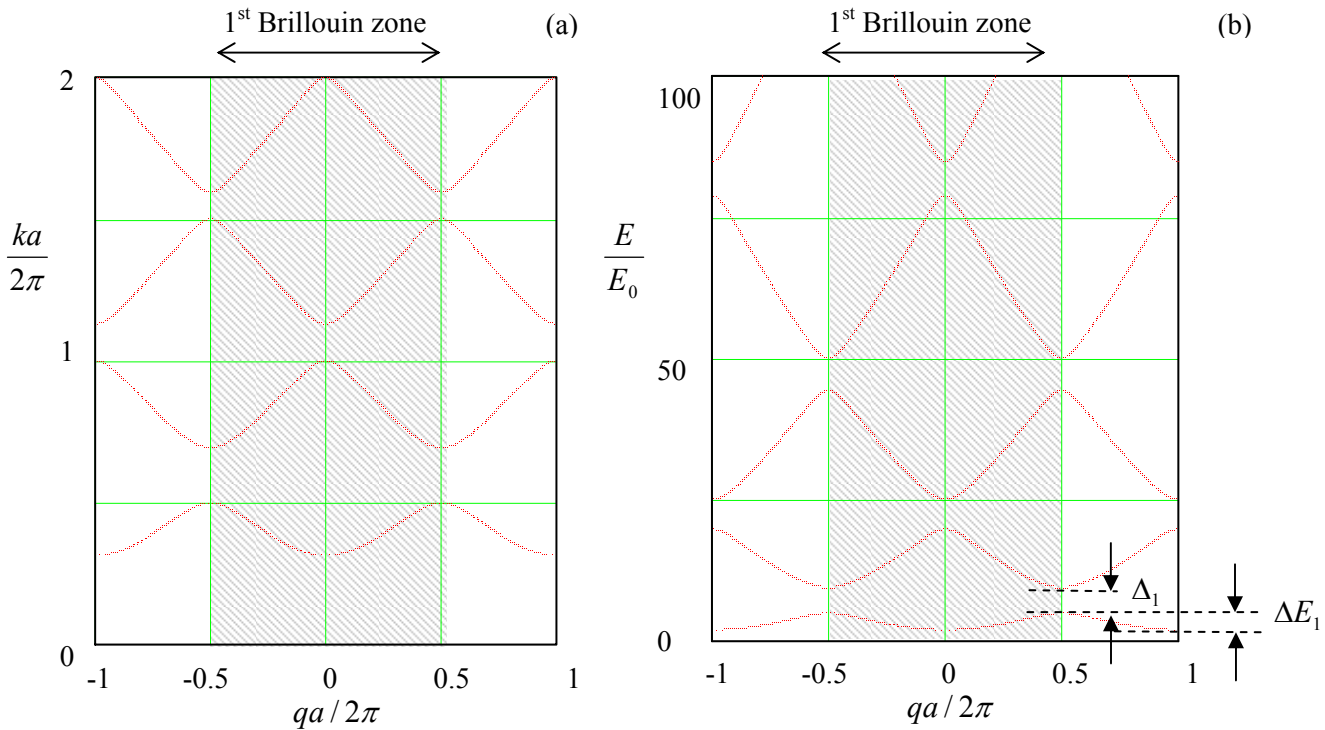


Fig. 2.26. (a) “Real” momentum k of a particle in the periodic delta-functional potential profile shown in Fig. 24, and (b) its energy $E = \hbar^2 k^2 / 2m$ (in units of $E_0 \equiv \hbar^2 / 2ma^2$), as functions of the quasi-momentum q , for a particular value ($\beta = 3$) of the dimensionless potential parameter $\beta \equiv (ka)\alpha = mWa/\hbar^2$. Arrows in the lower right corner of panel (b) illustrate the definition of the energy band (ΔE_n) and energy gap (Δ_n) widths.

⁵⁴ Perhaps a more important reason for taking q as the argument is that for motion in a general potential $U(x)$, particle’s momentum $\hbar k$ is not a constant of motion, while (according to the Bloch theorem), the quasi-momentum $\hbar q$ is.

However, maybe the most surprising fact, clearly visible in Fig. 26, is that there is a infinite number of energy bands, with different energies $E_n(q)$ for the same value of q . Mathematically, it is evident from Eq. (198) – see also Fig. 25. Indeed, for each value of qa there are two solutions ka to this equation on each period $\Delta(ka) = 2\pi$ – see also panel (a) in Fig. 26. Each of such solutions gives a different value of particle energy $E = \hbar^2 k^2 / 2m$. A continuous set of similar solutions for various qa forms a particular energy band.

Since the band theory is one of the most vital results of quantum mechanics, it is important to understand the physics of these different solutions - and hence of the whole band picture. For that, let us explore analytically two different potential strength limits. An important advantage of this approach is that both analyses may be carried out for an arbitrary periodic potential $U(x)$, rather than for the simplest model shown in Fig. 24.

(i) *Tight-binding approximation.* This approximation is sound when eigenenergy E_n is much lower than the height of the potential barriers separating the potential minima (serving as quantum wells) – see Fig. 27. As should be clear from our discussion in Sec. 6, the wavefunction is mostly localized in the classically allowed regions at points x_j of the potential energy minima - see the dashed lines in Fig. 27. Essentially the only role of coupling between these quantum well states (via tunneling through the separating barriers) is to establish certain phase shifts $\Delta\varphi = qa$ between the pairs of adjacent quasi-localized wavefunction “lumps” $u(x - x_j)$ and $u(x - x_{j+1})$.

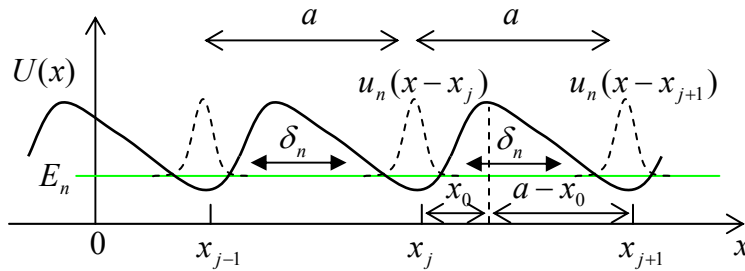


Fig. 2. 27. Tight binding approximation (schematically).

To describe this effect quantitatively, let us first return to the problem of two coupled wells considered in Sec. 6, and recast result (184) as

$$\Psi_n(x, t) = [a_R(t)\psi_R(x) + a_L(t)\psi_L(x)] \exp\left\{-i \frac{E_n}{\hbar} t\right\}, \quad (2.199)$$

where functions a_R and a_L oscillate sinusoidally in time:

$$a_R(t) = \cos \frac{\delta_n}{\hbar} t, \quad a_L(t) = i \sin \frac{\delta_n}{\hbar} t. \quad (2.200)$$

This evolution satisfies the following system of two equations whose structure reminds Eq. (1.59):

$$i\hbar \dot{a}_R = -\delta_n a_L, \quad i\hbar \dot{a}_L = -\delta_n a_R. \quad (2.201)$$

Later in the course (in Chapter 6) we will prove that such equations are indeed valid, in the tight-binding approximation, for any system of two coupled quantum wells. These equations may be readily generalized to the case of many similar coupled wells. Here, in this case, instead of Eq. (199), we evidently should write

$$\Psi_n(x, t) = \exp\left\{-i \frac{E_n}{\hbar} t\right\} \sum_j a_j(t) u_n(x - x_j), \quad (2.202)$$

where E_n are the eigenenergies, and u_n the eigenfunctions of each isolated well. In the tight binding limit, only the adjacent wells are coupled, so that instead of Eq. (201) we should write an infinite system of similar equations

$$i\hbar \dot{a}_j = -\delta_n a_{j-1} - \delta_n a_{j+1}, \quad (2.203)$$

for each well number j , where parameters δ_n describe the coupling between two adjacent quantum wells. Repeating the calculation outlined in the end of Sec. 6 for our new situation, we get the result essentially similar to the last form of Eq. (190):

$$\delta_n = \frac{\hbar^2}{m} u_n(x_0) \frac{du_n}{dx}(a - x_0), \quad (2.204)$$

Tight
binding
limit:
coupling
energy

where x_0 is the distance between the well bottom and the middle of the tunnel barrier on the right of it – see Fig. 27. The only substantial new feature of this expression in comparison with Eq. (190) is that the sign of δ_n alternates with the level number n : $\delta_1 > 0$, $\delta_2 < 0$, $\delta_3 > 0$, etc. Indeed, the number of “wiggles” (formally, zeros) of eigenfunctions $u_n(x)$ of any potential well increases as n – see, e.g., Fig. 1.7,⁵⁵ so that the difference of the exponential tails of the functions, sneaking under the left and right barriers limiting the well also alternates with n .

The infinite system of ordinary differential equations (203) allows one to explore a large range of important problems (such as the spread of the wavefunction that was initially localized in one well, etc.), but our main task now is to find its stationary states, i.e. the solutions proportional to $\exp\{-i(\varepsilon_n/\hbar)t\}$, where ε_n is a still unknown, q -dependent addition to the background energy E_n of n -th level. In order to satisfy the Bloch theorem (193) as well, such solution should have the form

$$a_j(t) = a \exp\left\{iqx_j - i \frac{\varepsilon_n}{\hbar} t + \text{const}\right\}, \quad (2.205)$$

where a is a constant. Plugging this solution into Eq. (203) and canceling the common exponent, we get

$$E = E_n + \varepsilon_n = E_n - \delta_n (e^{-iqa} + e^{iqa}) = E_n - 2\delta_n \cos qa, \quad (2.206)$$

Tight
binding
limit:
energy
bands

so that in this approximation, the energy band width ΔE_n (see Fig. 26b) equals $4|\delta_n|$.

Relation (206), whose validity is restricted to $|\delta_n| \ll E_n$, describes the particular lowest energy bands plotted in Fig. 26b reasonably well. (For larger β , the agreement would be even better.) So, this calculation explains what the energy bands really are – in the tight binding limit they are best interpreted as isolated well’s energy levels E_n , broadened into bands by the interwell interaction. Also, this result gives a clear proof that the energy band extremes correspond to $qa = 2\pi l$ and $qa = 2\pi(l + 1/2)$, with integer l . Finally, the sign alteration of the coupling coefficient δ_n (204) with number n explains why the energy maxima of one band are aligned, on the qa axis, with energy minima of the adjacent bands.

⁵⁵ Below, we will see several other examples of this behavior. This alternation rule is also in accordance with the Bohr-Sommerfeld quantization condition

(ii) *Weak-potential limit*. Surprisingly, the energy band structure is also compatible with a completely different physical picture that can be developed in the opposite limit. Let energy E be so high that the periodic potential $U(x)$ may be treated as a small perturbation. Naively, we would have the parabolic dispersion relation between particle's energy and momentum. However, if we are plotting energy as a function of q rather than k , we need to add $2\pi l/a$, with arbitrary integer l , to the argument. Let us show this by expanding all variables into the spatial Fourier series. For a periodic potential energy $U(x)$ such an expansion is straightforward:⁵⁶

$$U(x) = \sum_{l''} U_{l''} \exp\left\{-i \frac{2\pi x}{a} l''\right\}, \quad (2.207)$$

where the summation is over all integers l'' , from $-\infty$ to $+\infty$. However, for the wavefunction we should show due respect to the Bloch theorem (193). To understand how to proceed, let us define another function

$$u(x) \equiv \psi(x) e^{-iqx}, \quad (2.208)$$

and study its periodicity:

$$u(x+a) = \psi(x+a) e^{-iq(x+a)} = \psi(x) e^{-iqx} = u(x). \quad (2.209)$$

We see that the new function is a -periodic, and hence we can use Eqs. (208)-(209) to rewrite the Bloch theorem as

Bloch
theorem:
alternative
form

$$\psi(x) = u(x) e^{iqx}, \quad \text{with } u(x+a) = u(x). \quad (2.210)$$

Now it is safe to expand the periodic function $u(x)$ exactly as $U(x)$:

$$u(x) = \sum_{l'} u_{l'} \exp\left\{-i \frac{2\pi x}{a} l'\right\}, \quad (2.211)$$

so that, according to the Bloch theorem,

$$\psi(x) = e^{iqx} \sum_{l'} u_{l'} \exp\left\{-i \frac{2\pi x}{a} l'\right\} = \sum_{l'} u_{l'} \exp\left\{i \left(q - \frac{2\pi}{a} l'\right) x\right\}. \quad (2.212)$$

The only nontrivial part of plugging this expression into the stationary Schrödinger equation (61) is the calculation of the product term, using expansions (207) and (211):

$$U(x)\psi = \sum_{l', l''} U_{l''} u_{l'} \exp\left\{i \left(q - \frac{2\pi x}{a} (l' + l'')\right) x\right\}. \quad (2.213)$$

At fixed l' , we may change summation over l'' to that over $l \equiv l' + l''$ (so that $l'' = l - l'$), and write:

$$U(x)\psi = \sum_l \exp\left\{i \left(q - \frac{2\pi x}{a} l\right) x\right\} \sum_{l'} u_{l'} U_{l-l'}. \quad (2.214)$$

⁵⁶ The benefits of my unusual choice of the summation index (l'' instead of, say, l) will be clear in a few lines.

Now plugging Eqs. (212) (with index l' now replaced by l) and (214) into the stationary Schrödinger equation (61), and requiring the coefficients of each spatial exponent to match, we get an infinite system of linear equations for u_l :⁵⁷

$$\sum_{l'} U_{l-l'} u_{l'} = \left[E - \frac{\hbar^2}{2m} \left(q - \frac{2\pi}{a} l \right)^2 \right] u_l. \quad (2.215)$$

So far, this system is an equivalent alternative to the initial Schrödinger equation – and, by the way, is very efficient for fast numerical calculations, for virtually any potential strength, though in systems with tight binding it may require taking into account a large number of harmonics u_l . In the weak potential limit, i.e. if all the Fourier coefficients U_n are small,⁵⁸ we can complete all the calculation analytically.⁵⁹ Indeed, in the so-called 0th approximation we can ignore all U_n , so that in order to have at least one u_l different from 0, Eq. (215) requires that

$$E \rightarrow E_l \equiv \frac{\hbar^2}{2m} \left(q - \frac{2\pi l}{a} \right)^2. \quad (2.216)$$

(u_l itself should be obtained from the normalization condition). This result means that the dispersion relation $E(q)$ has an infinite number of similar quadratic branches numbered by integer l – see Fig. 28.

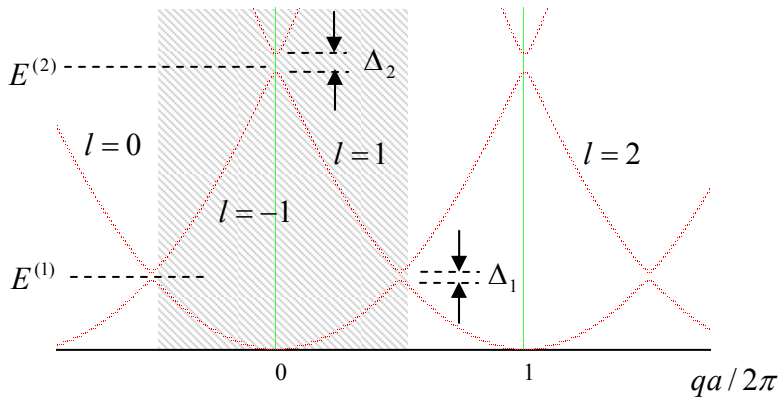


Fig. 2.28. 1D band picture in the weak potential case ($\Delta_n \ll E^{(n)}$). Shading shows the 1st Brillouin zone.

On any branch, the eigenfunction has just one Fourier coefficient, i.e. presents a monochromatic traveling wave

$$\psi_l \rightarrow u_l e^{ikx} = u_l \exp \left\{ i \left(q - \frac{2\pi l}{a} \right) x \right\}. \quad (2.217)$$

⁵⁷ Note that we have essentially proved that the Bloch wavefunction (210) is indeed a solution of Eq. (61), provided that the quasi-momentum q is selected in a way to make the system of linear equation (215) compatible, i.e. is a solution of its characteristic equation – see, e.g., Eq. (223) below.

⁵⁸ Besides the constant potential U_0 that, as we know from Sec. 2, may be included into energy in a trivial way, so that we may take $U_0 = 0$.

⁵⁹ This method is so powerful that its multi-dimensional version is not much more complex than the 1D version described here – see, e.g., Sec. 3.2 in the classical textbook by J. M. Ziman, *Principles of the Theory of Solids*, 2nd ed., Cambridge U. Press, 1979.

This fact allows us to rewrite Eq. (215) in a more transparent form

$$\sum_{l' \neq l} U_{l'-l} u_{l'} = (E - E_l) u_l, \quad (2.218)$$

that may be formally solved for u_l :

$$u_l = \frac{1}{E - E_l} \sum_{l' \neq l} U_{l'-l} u_{l'}. \quad (2.219)$$

If the Fourier coefficients U_n are nonvanishing but small, this formula shows that wavefunctions do acquire other Fourier components (besides the main one, with the index corresponding to the branch number), but these additions are all small, besides narrow regions near the points $E_l = E_{l'}$ where two branches (216) of the dispersion relation $E(q)$, with some specific numbers l and l' , cross. This happens when

$$\left(q - \frac{2\pi}{a} l \right) \approx - \left(q - \frac{2\pi}{a} l' \right), \quad (2.220)$$

i.e. at $q \approx q_m \equiv \pi m/a$ (with integer $m \equiv l + l'$)⁶⁰ corresponding to

$$E_l \approx E_{l'} \approx \frac{\hbar^2}{2ma^2} [\pi(l + l') - 2\pi l]^2 = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \equiv E^{(n)}, \quad (2.221)$$

with integer $n \equiv l - l'$. (Equation (221) shows that index n is just the number of the branch crossing on the energy scale – see Fig. 28.) In such a region, E has to be close to both E_l and $E_{l'}$, so that the denominator in just one of the infinite number of terms in Eq. (219) is very small, making the term substantial despite the smallness of U_n . Hence we can take into account only one term in each of the sums (written for l and l'):

$$\begin{aligned} U_{-n} u_{l'} &= (E - E_l) u_l, \\ U_n u_l &= (E - E_{l'}) u_{l'}. \end{aligned} \quad (2.222)$$

Taking into account that for any real function $U(x)$ the Fourier coefficients in series (207) have to be related as $U_{-n} = U_n^*$, Eq. (222) yields the following simple characteristic equation

$$\begin{vmatrix} E - E_l & -U_n^* \\ -U_n & E - E_{l'} \end{vmatrix} = 0, \quad (2.223)$$

with solution

$$E_{\pm} = E_{\text{ave}} \pm \left[\left(\frac{E_l - E_{l'}}{2} \right)^2 + U_n U_n^* \right]^{1/2}. \quad (2.224)$$

According to Eq. (216), close to the branch crossing point $q_m = \pi(l + l')/a$, the fraction participating in this result may be approximated as⁶¹

⁶⁰ Let me hope that the difference between this new integer and particle's mass, both called m , is absolutely clear from the context.

⁶¹ Physically, $\beta/\hbar = \hbar(n\pi/a)/m = \hbar k^{(n)}/m$ is just the velocity of a free classical particle with energy $E^{(n)}$.

$$\frac{E_l - E_{l'}}{2} \approx \gamma \tilde{q}, \quad \text{with } \gamma \equiv \left. \frac{dE_l}{dq} \right|_{q=q_m} = \frac{\pi \hbar^2 n}{ma} = \frac{2E^{(n)}}{\pi n}, \quad \text{and } \tilde{q} \equiv q - q_m, \quad (2.225)$$

while parameters $E_{\text{ave}} \equiv (E_l + E_{l'})/2 = E^{(n)}$ and $U_n U_n^* = |U_n|^2$ do not depend on $\tilde{q}$, i.e. the distance from the central point q_m . This is why Eq. (224) may be plotted as the famous *level anticrossing* (also called “avoided crossing”, or “intended crossing”, or “non-crossing”) *diagram* (Fig. 29), with the energy gap width Δ_n equal to $2|U_n|$, i.e. just double the magnitude of the n -th Fourier harmonic of the periodic potential $U(x)$. Such anticrossings are also clearly visible in Fig. 28 that shows the results of the exact solution of Eq. (198) for $\beta = 0.5$.⁶²

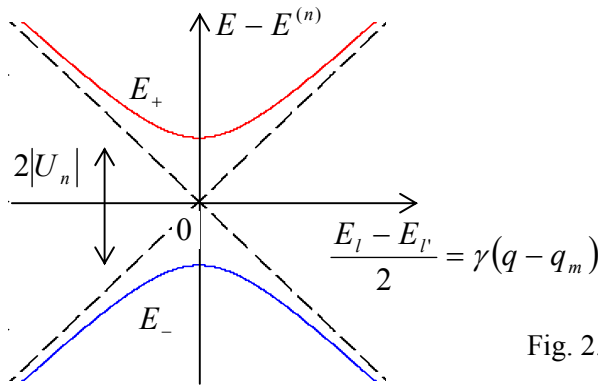


Fig. 2.29. Level anticrossing diagram.

We will run into the anticrossing diagram again and again in the course, notably at the discussion of spin. Such diagram characterizes any quantum systems with two weakly-interacting eigenstates with close energies. It is also repeatedly met in classical mechanics, for example at the calculation of eigenfrequencies of coupled oscillators.^{63,64} In our current case of the weak potential limit, the diagram describes the weak interaction of two sinusoidal de Broglie waves (216), with oppositely directed wave vectors, l and $-l'$, via the $(l - l')$ th (i.e. n th) Fourier harmonic of the potential profile $U(x)$. This effect exists also for the classical wave theory, and is known as the *Bragg reflection*, describing, for example, the 1D case of the wave reflection by a crystal lattice (Fig. 1.5) in the limit of weak interaction between the incident particles and the lattice.

Returning for the last time to our initial result – the band structure for the delta-functional $U(x)$ (Fig. 24), shown in Fig. 26, we may wonder how general it is, taking into account the peculiar properties of the delta-function approximation. A partial answer may be obtained from the band structure for two more realistic and relatively simple periodic functions $U(x)$: the sinusoidal potential (Fig. 30a) and the rectangular *Kronig-Penney potential* shown in Fig. 30b.

For the sinusoidal potential (Fig. 30a), with $U(x) = U_1 \cos(2\pi x/a)$, the stationary Schrödinger equation (61) takes the form

⁶² From that figure, it is also clear that in the weak potential limit, width ΔE_n of the n -th energy band is just $E^{(n)} - E^{(n-1)}$ – see Eq. (221). Note that this is exactly the distance between adjacent energy levels of the simplest 1D quantum well of infinite depth – cf. Eq. (1.77).

⁶³ See, e.g., CM Sec. 5.1 and in particular Fig. 5.2.

⁶⁴ Actually, we could obtain this diagram earlier in this section, for the system of two weakly coupled quantum wells (Fig. 23), if we assumed the wells to be slightly dissimilar.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U_1 \cos \frac{2\pi x}{a} \psi = E\psi. \quad (2.226)$$

By the introduction of dimensionless variables

$$\xi \equiv \frac{\pi x}{a}, \quad \alpha \equiv \frac{E}{E^{(1)}}, \quad 2\beta \equiv \frac{U_1}{E^{(1)}}, \quad (2.227)$$

where $E^{(1)}$ is defined by Eq. (221), Eq. (226) may be reduced to the canonical form of the well-known *Mathieu equation*⁶⁵

Mathieu
equation

$$\frac{d^2\psi}{d\xi^2} + (\alpha - 2\beta \cos 2\xi)\psi = 0. \quad (2.228)$$

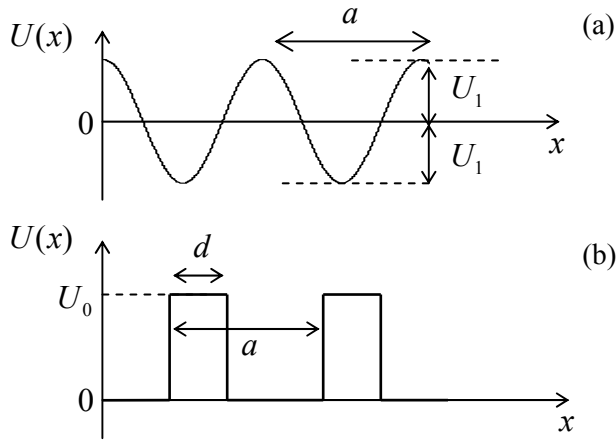


Fig. 2.30. Two simple periodic potential profiles: (a) the sinusoidal (“Mathieu”) potential and (b) the Kronig-Penney potential.

Figure 31 shows the so-called *characteristic curves* of the Mathieu equation, i.e. the relations between parameters α and β , corresponding to the energy band edges separating them from the adjacent bands. (Such curves may be readily calculated numerically, for example, using Eqs. (215) with the band-edge values $qa = 0$ and $qa = \pi$). In such “phase plane” plots, the detailed information about the energy dependence on the quasi-momentum is lost, but we already know from Fig. 26 that the dependence is not too eventful. The most remarkable feature of these plots is the fast (exponential) disappearance of the allowed energy bands at $2\beta > \alpha$ (in Fig. 31, above the red dashed line), i.e. at $E < U_1$. This may be readily explained by our tight-binding approximation result (206): as soon as the eigenenergy drops significantly below the potential maximum $U_{\max} = U_1$ (see Fig. 30a), quantum states in the adjacent potential wells are only connected by tunneling through the separating potential barriers, with exponentially small amplitudes δ_n – see Eq. (204).

On the other hand, the characteristic curves below the dashed line, i.e. at $2\beta < \alpha$, correspond to virtually free motion of the particle with energy E above $U_{\max} = U_1$. Naturally, in this region the energy bands rapidly expand while gaps virtually disappear. This could be expected from the weak potential limit analysis (see Fig. 28 and its discussion); however, based on that analysis one could expect that the

⁶⁵ This equation, first studied in the 1860s by É. Mathieu in the context of a rather practical problem of vibrating elliptical drumheads (!), has many other important applications in physics and engineering, notably including the parametric excitation of oscillations – see, e.g., CM Sec. 4.5.

energy gaps $\Delta_n \approx 2|U_n|$ would disappear more gradually. The fast decline of the gaps at $U_1 \rightarrow 0$ (i.e. $\beta \rightarrow 0$) in the Mathieu equation is an artifact of the sinusoidal potential $U(x)$, with no Fourier harmonics U_n above the first one. (In order to calculate the correct asymptotic behavior $\Delta_n \propto \beta^n$ at $\beta \rightarrow 0$, one needs to go beyond the first approximation we have used in the weak potential limit analysis.)

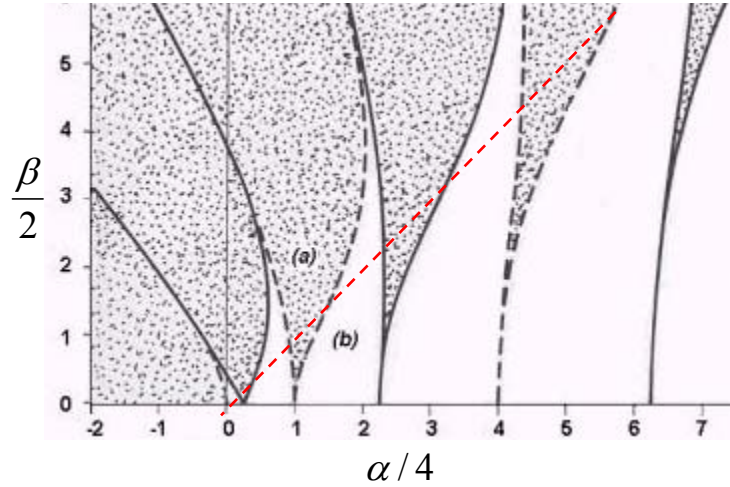


Fig. 2.31. Characteristic curves of the Mathieu equation. In application to the band theory, dotted regions correspond to the energy gaps, while regions between them, to energy bands. The red dashed line corresponds to condition $\alpha = 2\beta$, i.e. $E = U_1 \equiv U_{\max}$, separating the regions of tunneling and over-barrier motion. Figure adapted from <http://www.enm.bris.ac.uk/teaching/>.

If one wants to study the details of transition between the two limits in the 1D band theory without the artifacts of the delta-functional model shown in Fig. 24 (with infinite number of harmonics U_n independent of n) and of the Mathieu equation (with all $U_n = 0$ for $n \neq \pm 1$), the standard way is to examine the Kronig-Penney potential shown in Fig. 30b. For this potential, the characteristic equation may be readily derived using our rectangular barrier analysis in Sec. 3. For the case $E < U_0$, the result is the following natural generalization of Eq. (166):

$$\cos qa = \cosh \kappa d \cos k(a-d) + \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \sinh \kappa d \sin k(a-d), \quad (2.229)$$

where parameters k and κ are defined, as functions of E and U_0 , by Eqs. (62) and (65). In the opposite case $E > U_0$, one can use the same formula with the replacement (73). Plots $E(q)$, described by these formulas,⁶⁶ are very similar to those shown in Figs. 26b and 28 above. In order to see some difference, one needs to plot the characteristic curves $U_0(E)$. This may be done by taking $qa = 0$ and $qa = \pi$ (i.e. $\cos qa = \pm 1$) in Eq. (229), and solving the resulting transcendent equation for U_0 numerically. The curves are generally similar to those shown in Fig. 31, but, in accordance with Eq. (224), exhibit a more gradual decrease of energy gaps:

$$\Delta_n \rightarrow 2|U_n| \propto \frac{U_0}{n}, \quad \text{at } E \sim E^{(n)} \gg U_0. \quad (2.230)$$

To conclude this section, let me address the effect of periodic potential on the number of eigenstates in 1D systems of large but finite length $l \gg a, k^{-1}$. Surprisingly, the Bloch theorem makes the analysis of this problem elementary, for arbitrary $U(x)$. Indeed, let us assume that l is comprised of

⁶⁶ Such plots, for several particular values of parameters, may be found, for example, in Figs. 8.11-8.13 of E. Merzbacher's textbook cited above.

an integer number of periods a , and its ends are described by the similar boundary conditions – both assumptions evidently inconsequential for $l \gg a$ (such as a 1-cm-scale crystal with $\sim 10^8$ atoms along each direction). Then, according to Eq. (210), the boundary conditions impose, on the quasi-momentum q , exactly the same quantization condition as we had for k for a free 1D motion. Hence, instead of Eq. (1.94) we can write

$$dN = \frac{l}{2\pi} dq, \quad (2.231)$$

with the corresponding change of the summation rule:

$$\sum_q f(q) \rightarrow \frac{l}{2\pi} \int f(q) dq. \quad (2.232)$$

Hence, the density of states in 1D q -space, $dN/dq = l/2\pi$, does not depend on the potential profile at all! Note, however, that the profile does affect the density of states *on the energy axis*, dN/dE . As an extreme example, on the bottom and at the top of each energy band we have $dE/dq \rightarrow 0$, and hence

$$\frac{dN}{dE} = \frac{dN}{dq} / \frac{dE}{dq} = \frac{l}{2\pi} / \frac{dE}{dq} \rightarrow \infty. \quad (2.233)$$

This divergence (which survives in higher spatial dimensionalities as well) of the state density has important implications for the operation of several electron and optical devices, in particular semiconductor lasers.

2.8. Effective mass and the Bloch oscillations

The band structure of the energy spectrum has profound implications not only on the density of states, but also on the dynamics of particles in periodic potentials. In order to see that, let us consider the simplest case: motion of a wave packet consisting of Bloch functions (210), all in the same (say, n^{th}) energy band. Similarly to Eq. (27) for the a free particle, we can describe such a packet as

$$\Psi(x, t) = \int a_q u_q(x) e^{i[qx - \omega(q)t]} dq, \quad (2.234)$$

where the a -periodic functions $u(x)$, defined by Eq. (208), are now indexed to emphasize their dependence on the quasi-momentum, and $\omega(q) \equiv E_n(q)/\hbar$ is the function of q describing the shape of the corresponding energy band – see, e.g., Fig. 26b or Fig. 28. If the packet is narrow, i.e. the width δq of the distribution a_q is much smaller than all the characteristic scales of the dispersion relation $\omega(q)$, in particular π/a , we may simplify Eq. (234) exactly as we have done in Sec. 2 for a free particle, despite the presence of factors $u_q(x)$ under the integral. In the linear approximation of the Taylor expansion, we again get Eq. (32), but now with⁶⁷

$$v_{\text{gr}} = \left. \frac{d\omega}{dq} \right|_{q=q_0}, \quad \text{and} \quad v_{\text{ph}} = \left. \frac{\omega}{q} \right|_{q=q_0}, \quad (2.235)$$

⁶⁷ A generalization of this expression to the case of essential interband transitions is not difficult using the Heisenberg picture of quantum mechanics (which will be discussed in Chapter 4 of this course) - see, e.g., Sec. 55 in E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics, Part 2*, Pergamon, 1980.

where q_0 is the central point of the quasi-momentum distribution. Despite the formal similarity with Eq. (33) for the free particle, this result is much more eventful; for example, as evident from the dispersion relation's topology (see Figs. 26b, 28), the group velocity vanishes not only at $q = 0$, but at all values of q that are multiples of (π/a) , at the bottom and on the top of each energy band. At these points, packet's envelope does not move in either direction - though may keep spreading.⁶⁸

Even more fascinating phenomena take place if a particle in the periodic potential is the subject of an additional external force $F(t)$. (For electrons in a crystal lattice, this may be, for example, the Lorentz force of the applied electric and/or magnetic field.) Let the force be relatively weak, so that product Fa (i.e. the scale of energy increment from the additional force per one lattice period) is much smaller than the relevant energy scales the dispersion relation $E(q)$ – see Fig. 26b:

$$Fa \ll \Delta E_n, \Delta_n. \quad (2.236)$$

This relation allows one to neglect the force-induced interband transitions, so that the wave packet (234) includes the Bloch eigenfunctions belonging to only one (initial) energy band at all times. For the time evolution of its center q_0 , theory yields⁶⁹ an extremely simple equation of motion

$$\dot{q}_0 = \frac{1}{\hbar} F(t). \quad (2.237)$$

Time
evolution
of quasi-
momentum

This equation is physically very transparent: it is essentially the 2nd Newton law for the time evolution of the quasi-momentum $\hbar q$ under the effect of the additional force $F(t)$ only, excluding the periodic force $-\partial U(x)/\partial x$ of the background potential $U(x)$. This is very natural, because $\hbar q$ is essentially the particle's momentum averaged over potential's period, and the periodic force effect drops out at such an averaging.

Despite the simplicity of Eq. (237), the results of its solution may be highly nontrivial. First, let us use Eqs. (235) and (237) find the instant *group acceleration* of the particle (i.e. the acceleration of its wave packet's envelope):

$$a_{\text{gr}} \equiv \frac{dv_{\text{gr}}}{dt} = \frac{d}{dt} \frac{d\omega(q_0)}{dq_0} = \frac{d}{dq_0} \frac{d\omega(q_0)}{dq_0} \frac{dq_0}{dt} = \frac{d^2\omega(q_0)}{dq_0^2} \frac{dq_0}{dt} = \frac{1}{\hbar} \frac{d^2\omega}{dq^2} \Big|_{q=q_0} F(t). \quad (2.238)$$

This means that the second derivative of the dispersion relation plays the role of the effective reciprocal mass of the particle:

$$m_{\text{ef}} = \frac{\hbar}{d^2\omega/dq^2} = \frac{\hbar^2}{d^2E/dq^2}. \quad (2.239)$$

Effective
mass

For the particular case of a free particle, described by Eq. (216), this expression is reduced to the original (and constant) mass m , but generally the effective mass depends on the wave packet's momentum. According to Eq. (239), at the bottom of any energy band, m_{ef} is always positive, but depends on the strength of particle's interaction with the periodic potential. In particular, according to Eq. (206), in the tight binding limit, the effective mass is very large:

⁶⁸ For a Gaussian packet, the spreading is described by Eq. (39), with the replacement $k \rightarrow q$; it is curious that at the inflection points with $d^2\omega/dq^2 = 0$ (which are present in each energy band) the packet does not spread.

⁶⁹ The proof of Eq. (237) is not difficult, but becomes more compact in the bra-ket formalism, to be discussed in Chapters 4 and 5. This is why I recommend the proof to the reader as an exercise after reading those two chapters.

$$|m_{\text{ef}}|_{q=(\pi/a)n} = \frac{\hbar^2}{2\delta_n a^2} = m \frac{E^{(1)}}{\pi^2 \delta_n} \gg m. \quad (2.240)$$

On the contrary, in the weak potential limit, the effective mass is close to m at most points of each energy band, but at the edges of the (narrow) bandgaps it is much smaller. Indeed, expanding Eq. (224) in the Taylor series near point $q = q_m$, we get

$$E_{\pm}|_{E \approx E^{(n)}} \approx \pm |U_n| \pm \frac{1}{2|U_n|} \left(\frac{dE_l}{dq} \right)_{q=q_m}^2 \tilde{q}^2 = \pm |U_n| \pm \frac{\beta^2}{2|U_n|} \tilde{q}^2, \quad (2.241)$$

where β and $\tilde{q}$ are defined by Eq. (225), so that

$$|m_{\text{ef}}|_{q=q_m} = |U_n| \frac{\hbar^2}{\beta^2} = m \frac{|U_n|}{2E^{(n)}} \ll m. \quad (2.242)$$

The effective mass effects in real solids may be very significant. For example, the charge carriers in the ubiquitous field-effect transistors of silicon integrated circuits have $m_{\text{ef}} \approx 0.19 m_e$ in the lowest normally-empty energy band (traditionally called the *conduction band*), and $m_{\text{ef}} \approx 0.98 m_e$ in the lower, normally-filled *valence band*. In some semiconducting compounds the conduction-band electron mass may be even smaller - down to $0.0145 m_e$ in InSb!

However, the absolute value of the effective mass is not the most surprising effect. The more shocking corollary of Eq. (239) is that on the top of each energy band the effective mass is *negative* – please revisit Figs. 26, 28, and 29 again. This means that the particle (or more strictly its wave packet's envelope) is accelerated in the direction *opposite* to the force. This is exactly what electronic engineers, working with electrons in semiconductors, call *holes*, characterizing them by *positive mass* and *positive charge*. If the particle does not leave a close vicinity of the energy band's top (say, due to scattering effects), such flip of signs does not lead to an error, because the Lorentz force is proportional to electron's charge ($q = -e$), so that particle's acceleration a_{gr} is proportional to ratio (q/m_{ef}) .⁷⁰

However, at some phenomena the usual image of a hole as a particle with $q > 0$ and $m_{\text{ef}} > 0$ is unacceptable. For example, let us form a narrow wave packet at the bottom of the lowest energy band,⁷¹ and then exert on it a constant force $F > 0$ – say, due to a constant external electric field directed along axis x . According to Eq. (237), this would lead to a linear growth of q_0 in time, so that in the quasi-momentum space, the packet's center would slide, with constant speed, along the q axis – see Fig. 32a. Close to the energy band bottom, this motion would correspond to a positive effective mass (possibly, somewhat larger than the genuine particle's mass m), and hence be close to free particle's acceleration. However, as soon as q_0 has reached the inflection point, where $d^2 E_l / dq^2 = 0$, the effective mass, and hence acceleration (238) change signs to negative, i.e. the packet starts to slow down (in the direct space

⁷⁰ The language is which the hole has a positive charge and mass has an additional convenience for states on the top of the valence band whose single-particle states are normally filled. Then the simplest, single-particle excitation of this multi-particle ground state may be created by giving one electron enough energy to lift it to a reference (e.g., Fermi-energy) level E_F that is, by definition of the valence band, is higher than all values $E(q)$. Then it is natural to prescribe to the *excitation* a positive mass m_{ef} , because the energy $\Delta E = E_F - E(q)$ necessary for the excitation *grows* with the deviation of q from q_m .

⁷¹ Intuition tells us (and statistical physics duly confirms :-)) that this may be readily done, for example, by weakly coupling the system to a low-temperature environment, and letting it to relax to the lowest possible energy.

x) while still moving ahead in the quasi-momentum space. Finally, at the energy band's top the particle stops at certain $x_{\max}$, while continuing to move in the q -space.

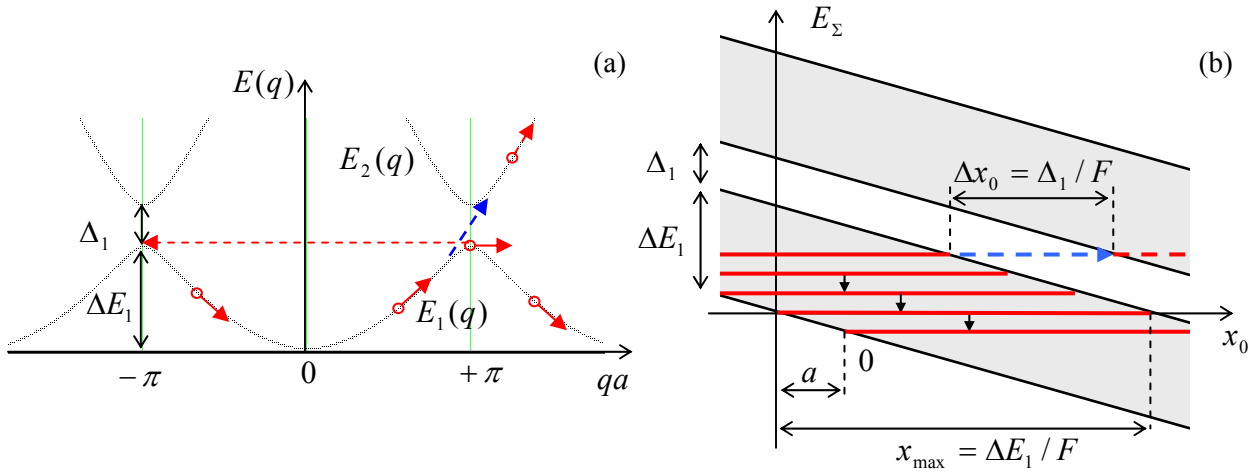


Fig. 2.32. The Bloch oscillations (red lines) and the Landau-Zener tunneling (blue arrows) within: (a) the time-domain picture, and (b) the energy-domain picture. On panel (b), the tilted gray strips show the allowed energy bands, and the bold red lines, the Wannier-Stark ladder.

Now we have two alternative ways to look at the further time evolution of the wave packet. From the extended zone picture (which is the simplest for this analysis, see Fig. 32a),⁷² we may say that the particle crosses the 1st Brillouin zone boundary and starts going forward in q , i.e. down the lowest energy band. According to Eq. (235), this region (up to the next inflection point) corresponds to a negative group velocity. After q_0 has reached the next minimum of the energy band at $qa = 2\pi$, the whole process repeats again (and again, and again).

These are the famous *Bloch oscillations* – the effect that was predicted (by the same F. Bloch) as early as in 1929, but evaded experimental observation until the 1980s - see below. Their time period may be readily found from Eq. (237):

$$\Delta t_B = \frac{\Delta q}{dq/dt} = \frac{2\pi/a}{F/\hbar} = \frac{2\pi\hbar}{Fa}, \quad (2.243)$$

so that the Bloch oscillation frequency

$$\omega_B \equiv \frac{2\pi}{\Delta t_B} = \frac{Fa}{\hbar}. \quad (2.244) \quad \text{Bloch oscillations: frequency}$$

The direct-space motion of the wave packet's center $x_0(t)$ during the Bloch oscillation process may be analyzed by integrating Eq. (235) over some time interval Δt :

⁷² This phenomenon may be also discussed from the point of view of the reduced zone picture, but then it requires the introduction of instant jumps between the Brillouin zone boundary points (see the dashed red line in Fig. 32) that correspond to physically equivalent states of the particle. Evidently, this language is more artificial.

$$\Delta x_0(t) = \int_0^{\Delta t} v_{\text{gr}} dt = \int_0^{\Delta t} \frac{d\omega(q_0)}{dq_0} dt = \int_0^{\Delta t} \frac{d\omega(q_0)}{dq_0} / dt = \frac{\hbar}{F} \int_{t=0}^{t=\Delta t} d\omega = \frac{\hbar}{F} \Delta\omega(q_0). \quad (2.245)$$

If interval Δt is equal to the Bloch oscillation period Δt_B (234), the initial and final moments of $E(q_0) = \hbar\omega(q_0)$ are equal, giving $\Delta x_0 = 0$: in the end of the period, the wave packet returns to its initial position. However, if we carry this integration only from the smallest to the largest values of $\omega(q_0)$, i.e. the points where the group velocity vanishes, we get the oscillation swing

Bloch
oscillations:
spatial
swing

$$\Delta x_{\text{max}} = \frac{\hbar}{F} (\omega_{\text{max}} - \omega_{\text{min}}) = \frac{\Delta E_1}{F}. \quad (2.246)$$

This simple result may interpreted using an alternative energy diagram (Fig. 32b) that results from the following arguments. The additional force F may be described not only via the 2nd Newton law version (237), but, alternatively, by its contribution $U_F = -Fx$ to the total (“Gibbs”⁷³) potential energy

$$U_{\Sigma}(x) = U(x) - Fx \quad (2.247)$$

of the system. The direct solution of the Schrödinger equation (61) with such potential may be hard to find, but if the force is weak in the sense of Eq. (236), as we are assuming now, one can argue that our quantum-mechanical treatment including the periodic potential $U(x)$ should be still correct, if the second term in Eq. (247) is considered as a constant at the wave packet width scale δx , but dependent on position x_0 of the packet’s center. In this approximation, the total energy of the wave packet may be found as

$$E_{\Sigma} = E(q_0) - Fx_0. \quad (2.248)$$

In a plot of such energy as a function of x_0 (Fig. 32b), the information on energy dependence on q_0 is lost, but we already know it is rather uneventful, and well characterized by the position of band-gap edges on the energy axis.⁷⁴ In this representation, the Bloch oscillations of a relatively wide ($\delta x \gg a$) wave packet should keep the full energy E_{Σ} constant, i.e. follow a horizontal line in Fig. 32b, limited by the classical turning points corresponding to the bottom and the top of the allowed energy band. The distance Δx_{max} between these point is evidently given by Eq. (246).

Besides this second look at the oscillation swing result, the total energy diagram shown in Fig. 32b enables one more remarkable result. Let a wave packet be so narrow in the momentum space ($\delta q \rightarrow 0$) that $1/q \gg \Delta x_{\text{max}}$, then the horizontal line segment in Fig. 32b presents the spatial extension of the eigenfunction of the Schrödinger equation with potential (247). But this equation is evidently invariant with respect to the following simultaneous translation in coordinate and energy:

$$x \rightarrow x + a, \quad E \rightarrow E - Fa. \quad (2.249)$$

Wannier-
Stark
ladder

This means that it is satisfied with an infinite set of similar solutions, each corresponding to one of the horizontal red lines shown in Fig. 32b. This is the famous *Wannier-Stark ladder*, with the step height

$$\Delta E_s = Fa. \quad (2.250)$$

⁷³ See, e.g., CM Sec. 1.5.

⁷⁴ In semiconductor device physics and engineering, such plots are called the *band edge diagrams*, and are the virtually unavoidable components of any discussion or publication.

The importance of this alternative representation of the Bloch oscillations is due to the following fact. In most experimental realizations, the power of radiation at frequency (244), that may be extracted from the oscillations by their electromagnetic coupling to an external detector, is very low, so that their direct detection presents a hard problem.⁷⁵ However, let us apply to a Bloch oscillator an additional rf field at frequency $\omega \sim \omega_B$. As these frequencies are brought close together, the external signal should synchronize (“phase lock”) Bloch oscillations,⁷⁶ resulting in certain observable changes – for example, a resonant absorption of the external radiation. Now let us notice that Eqs. (244) and (250) yield the following remarkable relation:

$$\Delta E_S = \hbar \omega_B. \quad (2.251)$$

This means that the resonant phenomena at $\omega \approx \omega_B$ allow for an alternative (but equivalent) interpretation – as the result of rf-induced transitions⁷⁷ between the steps of the Wannier-Stark ladder! (Such occasions when two very different languages may be used for the interpretation of the same phenomenon is one of the most beautiful features of physics.)

This effect has been used for the first experimental confirmation of the Bloch oscillation theory. For this purpose, the natural periodic structures, solid state crystals, are inconvenient due to their very small period $a \sim 10^{-10}$ m. Indeed, according to Eq. (244), such structures require very high forces F (and hence high electric fields $\mathcal{E} = F/e$) to bring ω_B to an experimentally convenient range. This problem has been overcome by fabricating artificial periodic structures (*superlattices*) of certain semiconductor compounds, such as $\text{Ga}_{1-x}\text{Al}_x\text{As}$ with various degrees x of gallium to aluminum atom replacement, whose layers may be grown over each other epitaxially, i.e., without very few crystal structure violations. These superlattices, with periods $a \sim 10$ nm, has allowed a clear observation of resonant effects at $\omega \approx \omega_B$, and hence the measurement of the Bloch oscillation frequency, in particular its proportionality to the applied dc electric field, predicted by Eq. (244).⁷⁸

Very soon after this observation, the Bloch oscillations have been observed in small Josephson junctions.⁷⁹ Since this experiment involved two important conceptual issues, let me discuss it in a little bit more detail. As was discussed in Sec. 2.3, the Josephson junction dynamics may be reasonably well described by two simple equations (54) and (55). They may be combined to calculate the work of an external voltage source at Josephson phase change between arbitrary initial (φ_{ini}) and final (φ_{fin}) values, as the integral of its power IV over the time interval Δt of the change:

$$\text{work} = \int_{\Delta t} IV dt = \int_{\Delta t} (I_c \sin \varphi) \left(\frac{\hbar}{2e} \frac{d\varphi}{dt} \right) dt = \frac{\hbar I_c}{2e} \int_{\varphi_{\text{ini}}}^{\varphi_{\text{fin}}} \sin \varphi d\varphi = -\frac{\hbar I_c}{2e} (\cos \varphi_{\text{fin}} - \cos \varphi_{\text{ini}}). \quad (2.252)$$

We see that the work depends only on the initial and final values of φ (but not on the law phase evolution in time), i.e. may be presented as the difference $U(\varphi_{\text{fin}}) - U(\varphi_{\text{ini}})$, where function

⁷⁵ In systems with many independent particles (such as semiconductors), the detection problem is exacerbated by phase incoherence of the Bloch oscillations performed by each particle. This drawback is absent in atomic Bose-Einstein condensates whose Bloch oscillations (in a periodic potential created by standing optical waves) were eventually observed by M. Ben Dahan *et al.*, *Phys. Rev. Lett.* **76**, 4508 (1996).

⁷⁶ A simple analysis of phase locking of a classical oscillator may be found, e.g., in CM Sec. 4.4.

⁷⁷ A qualitative theory of such transitions will be discussed in Sec. 6.6 and then in Chapter 7.

⁷⁸ E. Mendez *et al.*, *Phys. Rev. Lett.* **60**, 2426 (1988).

⁷⁹ L. Kuzmin and D. Haviland, *Phys. Rev. Lett.* **67**, 2890 (1991).

Josephson
coupling
energy

$$U(\varphi) = -E_J \cos \varphi + \text{const}, \quad \text{with } E_J \equiv \frac{\hbar I_C}{2e}, \quad (2.250)$$

may be interpreted as the potential energy of the junction (if we consider the Josephson phase as a generalized coordinate). This energy apart, the Josephson junction, as a system of two close, nearly isolated (super)conductors, has a certain capacitance C and the associated electrostatic energy $E_C = CV^2/2$. Using Eq. (54) again, we may present it as

$$E_C = \frac{C}{2} V^2 = C \left(\frac{\hbar}{2e} \right)^2 \left(\frac{d\varphi}{dt} \right)^2. \quad (2.251)$$

This means that from the point of view at phase φ as a generalized coordinate, E_C should be considered the kinetic energy of the system, whose dependence on the generalized velocity $d\varphi/dt$ is similar to that of a 1D mechanical particle, with an effective mass⁸⁰

$$m_J = C \left(\frac{\hbar}{2e} \right)^2. \quad (2.252)$$

Hence the total energy of the junction, $E_C + U(\varphi)$, is formally similar to that of a 1D nonrelativistic particle in the sinusoidal potential with the φ -axis period $a_J = 2\pi$.

However, before using the results of the 1D band theory to this system, we have to resolve one paradox (that was the subject of a lively discussion just about 30 years ago). When we develop the band theory, we imply that its translation by period a is (in principle) measurable, i.e. particle positions x and $(x + a)$ are distinguishable – otherwise Eq. (193) with $q \neq 0$ would not have much sense. For a mechanical particle this assumption is very plausible, but less so for a Josephson junction. Indeed, for example, if we change φ by $a_J = 2\pi$ via changing the phase of one of superconductors, say φ_1 (Fig. 3) by 2π , then its wavefunction becomes $|\psi| \exp\{i(\varphi_1 + 2\pi)\} = |\psi| \exp\{i\varphi_1\}$, and it is not immediately clear whether these two states may be distinguished. In order to resolve this contradiction, it is sufficient to have a look at Eq. (54). It shows that if φ changes in time by 2π (say, by a fast ramp-up), voltage V across the junction exhibits a pulse with “area”

SFQ
pulse

$$\int V(t) dt = \frac{\hbar}{2e} \int \frac{d\varphi}{dt} dt = \frac{\hbar}{2e} \int d\varphi = \frac{\hbar}{2e} 2\pi = \frac{h}{2e} \approx 2 \times 10^{-15} \text{ V} \cdot \text{s}. \quad (2.253)$$

Such *single-flux-quantum* (SFQ) pulses⁸¹ not only may be measured experimentally, but even have been used for signaling and ultrafast (sub-THz) computation, to the best of my knowledge still keeping the absolute records for the highest speed and smallest energy consumption at computation.⁸²

Hence, the 2π -shifts of phase φ are measurable, and in the absence of dissipation the Josephson junction dynamics is indeed similar to that of a 1D particle in a periodic (sinusoidal) potential, and its energy spectrum forms energy bands and gaps described by the Mathieu equation – see Fig. 31. Experimentally, the easiest way to verify this picture is to measure the corresponding Bloch oscillations

⁸⁰ Of course, the dimensionality of m_{eff} so defined is different from kg.

⁸¹ This term has originated from the fact that the right-hand part of Eq. (253) equals to the single quantum unit (Φ_0) of the magnetic flux in superconductors – see Sec. 3.1 below.

⁸² See, e.g., P. Bunyk *et al.*, *Int. J. on High Speed Electronics and Systems* **11**, 257 (2001).

induced by an external current $I_{\text{ex}}(t)$. In order to find the frequency of these oscillations, it is sufficient to replace Eq. (237), which expresses the 2nd Newton law averaged over period a of potential $U(x)$, with the charge balance equation

$$\frac{dQ}{dt} = I_{\text{ex}}(t), \quad (2.254)$$

where Q is the “quasi-charge”⁸³, i.e. the electric charge of the capacitor averaged over the period 2π of the periodic potential $U(\varphi)$. (Notice that at such averaging, current (55) is averaged out from the equation, so that it affects the phenomena “only” via its contribution to the energy band structure.)

Since the Josephson-junction analog of the genuine wave number $k = m(dx/dt)/\hbar$ of a particle is

$$k_J = \frac{m_J}{\hbar} \frac{d\varphi}{dt} = \frac{m_J}{\hbar} \frac{2e}{\hbar} V = \frac{CV}{2e}, \quad (2.255)$$

and CV is the genuine charge on the capacitor, the analog of q (the quasi-momentum divided by $\hbar$) may be obtained just by the replacement of that product with quasi-charge Q :

$$q_J = \frac{Q}{2e}. \quad (2.256)$$

Comparing this expression with Eq. (254), we see that q_J obeys the following equation of motion:

$$\frac{dq_J}{dt} = \frac{I_{\text{ex}}(t)}{2e}. \quad (2.257)$$

so that the role of force F is now played by $F_J = \hbar I/2e$. Hence if $I_{\text{ex}}(t) = \text{const} = \bar{I}$, we can use Eq. (244) with that replacement, and also $a \rightarrow a_J = 2\pi$, to get

$$f_B \equiv \frac{\omega_B}{2\pi} = \frac{1}{2\pi} \frac{F_J a_J}{\hbar} = \frac{\bar{I}}{2e}. \quad (2.258)$$

Bloch
oscillations
in super-
conductivity

This very simple result has the following physical sense.⁸⁴ In the quantum operation mode, the junction is recharged by the external current, following Eq. (256), until its electric charge reaches e (i.e. $q_J a_J = (Q/2e)2\pi$ reaches π - see Fig. 32a); then one Cooper pair passes through the junction changing its charge to $e - (2e) = -e$, with the same charging energy (251) - the process analogous to crossing the border of the 1st Brillouin zone; then the process repeats again and again. It is remarkable that Eq. (258), describing the frequency of such *quantum* property of the Josephson phase φ as its Bloch oscillations, does not include the Planck constant, while Eq. (56), describing the classical motion of φ , does.

In this context, one may wonder which of these two types of oscillations would a dc-biased Josephson junction generate. For the dissipation-free junction, the answer is: the Bloch oscillations (258) with frequency proportional to dc current. However, any practical junction has some energy losses that may be (approximately) described by a certain Ohmic conductance G connected in parallel to the

⁸³ Eq. (254) tells us that quasi-charge Q has the simple physical sense of the external electric charge being inserted into the junction by the external current I_{ex} - just like the physical sense of quasi-momentum $\hbar q$ of a mechanical particle, according to Eq. (237), is the contribution to particle's momentum by the external force F .

⁸⁴ D. Averin *et al.*, *Sov. Phys. - JETP* **61**, 407 (1985).

junction. Very luckily for Dr. Josephson and his Nobel Prize, it is much easier to fabricate and test junctions with $G \gg 1/R_Q$, where R_Q is the so-called *quantum unit of resistance*

$$R_Q \equiv \frac{\pi\hbar}{2e^2} \approx 6.45 \text{ k}\Omega, \quad (2.259)$$

Quantum
unit of
resistance

the fundamental constant that jumps out at analysis of several other effects as well – see, e.g., Sec. 3.2. As will be discussed in Chapter 7, such high energy losses provide what is called *dephasing* – the suppression of the quantum coherence between different quantum states of the system – in our current case, between the wavefunctions $u(\varphi - 2\pi j)$ localized at different minima of the periodic potential $U(\varphi)$, and thus make the dynamics of the Josephson phase φ virtually classical, obeying equations (54) and (55). As we have seen in Sec. 2, dc biasing of such a junction leads to Josephson oscillations with frequency (56) proportional to the applied dc voltage.

2.9. Landau-Zener tunneling

All the Bloch oscillation discussion in the last section was based on the premise that the particle stays within one (say, the lowest) energy band. However, just a single look at Fig. 32 shows that this assumption becomes unrealistic if the energy gap separating this band from the next one becomes very small, $\Delta_1 \rightarrow 0$. Indeed, in the weak potential approximation, that is adequate in this limit, at $|U_1| \rightarrow 0$, the two dispersion curve branches (216) cross without any interaction, so that if our particle (the wave packet) is driven to approach that point, it should continue to move up in energy – see the dashed blue arrow in Fig. 32a. Similarly, in the “energy-domain” presentation shown in Fig. 32b, it is intuitively clear that at $\Delta_1 \rightarrow 0$, the particle residing at one of the steps of the Wannier-Stark ladder should be able to somehow overcome the vanishing spatial gap $\Delta x_0 = \Delta_1/F$ and to leak into the next band – see the horizontal dashed blue arrow on that panel.

This process, called the *Landau-Zener* (or “interband”, or “band-to-band”) *tunneling*⁸⁵ is indeed possible. In order to analyze it, let us first take $F = 0$, and consider what happens if a quantum particle described by an x -long (i.e. E -narrow) wave packet is incident from the free space upon a periodic structure of a large but finite length $l \gg a$. If packet’s energy E is within one of the energy bands, it may evidently propagate through the structure (though may be partly reflected from its front end). The corresponding quasi-momentum may be found by solving the dispersion relation for q ; for example, in the weak-potential limit, Eq. (224), which is valid near the gap, yields

$$q = q_m + \tilde{q}, \quad \tilde{q} = \pm \frac{1}{\gamma} \left[\tilde{E}^2 - |U_n|^2 \right]^{1/2}, \quad \text{where } \tilde{E} \equiv E_{\pm} - E^{(n)}, \quad (2.260)$$

and γ is given by the second of Eqs. (225).

Now, if energy E corresponds to one of the energy gaps Δ_n , the propagation is impossible, so that the packet is completely reflected back. However, our analysis of the potential step problem in Sec. 3 implies that the wavefunction would still have an exponential tail protruding into the periodic structure and decaying on some length δ – see Eq. (67). Indeed, a review of the calculation leading to Eq. (260)

⁸⁵ It was predicted independently by L. D. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932) and C. Zener, *Proc. R. Soc. London A* **137**, 696 (1932).

shows that they remain valid within the gap as well, if the quasi-momentum is understood as a purely imaginary number:

$$\tilde{q} \rightarrow \pm i\kappa, \quad \text{where } \kappa \equiv \frac{1}{\gamma} \left[|U_n|^2 - \tilde{E}^2 \right]^{1/2}, \quad \text{for } \tilde{E}^2 \leq |U_n|^2. \quad (2.261)$$

With such contribution, the Bloch solution (193b) indeed describes an exponential decay of the wavefunction at length $\delta = 1/\kappa$.

Now returning to the effects of weak force F in the energy-domain approach, presented by Eq. (248) and illustrated in Fig. 32b, we may recast Eq. (261) as

$$\kappa \rightarrow \kappa(x) = \frac{1}{\gamma} \left[|U_n|^2 - (F\tilde{x})^2 \right]^{1/2}, \quad (2.262)$$

where $\tilde{x}$ is particle's (i.e. wave packet center's) deviation from the mid-gap point. Thus the gap has created a potential barrier of a finite width $\Delta x_0 = 2F/|U_n|$, through which the wave packet may tunnel with a finite probability. As we already know, in the WKB approximation (in our case requiring $\kappa\Delta x_0 \gg 1$) this probability is just the tunnel barrier's transparency T , which may be calculated from Eq. (117):

$$-\ln T = 2 \int_{\kappa(x)^2 > 0} \kappa(x) dx = \frac{2}{\gamma} \int_{-x_c}^{x_c} \left[|U_n|^2 - (F\tilde{x})^2 \right]^{1/2} d\tilde{x} = \frac{2|U_n|}{\gamma} 2x_c \int_0^1 (1 - \xi^2)^{1/2} d\xi. \quad (2.263)$$

where $\pm x_c \equiv \pm \Delta x_0/2 = \pm F/|U_n|$ are the classical turning points. Working out this simple integral (which may be viewed upon as the quarter of the unit circle's area, and hence equal to $\pi/4$), we get

$$T = \exp \left\{ -\frac{\pi |U_n|^2}{\gamma F} \right\}. \quad (2.264)$$

Landau-Zener
tunneling
probability

This famous result was obtained by Landau and Zener in a more complex way, whose advantage is a constructive proof that Eq. (264) is valid for arbitrary relation between γF and $|U_n|^2$, i.e. arbitrary T , while our simple derivation was limited to the WKB approximation, i.e. to $T \ll 1$.⁸⁶

Returning to Eq. (225) and (237), we can rewrite the product γF participating in Eq. (264) as

$$\gamma F = \frac{1}{2} \left| \frac{d(E_l - E_{l'})}{dq_0} \right|_{E_l=E_{l'}=E_n} \hbar \frac{dq_0}{dt} = \frac{\hbar}{2} \left| \frac{d(E_l - E_{l'})}{dt} \right|_{E_l=E_{l'}=E_n} = \frac{\hbar u}{2}, \quad (2.265)$$

where u has the meaning of the “speed” of the energy level crossing in the absence of the gap. Hence, Eq. (264) may be presented in a form

$$T = \exp \left\{ -\frac{2\pi |U_n|^2}{\hbar u} \right\}, \quad (2.266)$$

⁸⁶ Note that Eq. (264) is still limited to the hyperbolic dispersion relation, i.e. (in the band theory) to the weak potential limit. In the opposite, tight-binding limit, the interband tunneling may be treated as an excitation of the upper band states by sinusoidal Bloch oscillations, and is completely suppressed at $\hbar\omega_B < \Delta_1$.

that is more physically transparent.⁸⁷ Indeed, the fraction $2|U_n|/u = \Delta_n u$ gives the time scale Δt of energy's crossing the gap region, and according to the Fourier transform, its reciprocal, $\omega_{\max} \sim 1/\Delta t$ gives the upper cutoff of frequencies involved in the Bloch oscillation process. Hence Eq. (266) means that

$$-\ln T \approx \frac{\Delta_n}{\hbar \omega_{\max}}. \quad (2.267)$$

This formula allows us to interpret the Landau-Zener tunneling as for system's excitation across the energy gap Δ_n , by the maximum energy quantum $\hbar \omega_{\max}$ available from the Bloch oscillation process.

The interband tunneling is an important ingredient of several physical phenomena and even some practical devices, for example the *tunneling* (or “Esaki”) *diodes*. This simple device is just a junction of two semiconductor electrodes, one of them is so strongly *n*-doped by electron donors that the additional electrons form a degenerate Fermi gas at the bottom of the conduction band. Similarly, the opposite electrode is *p*-doped so strongly that the Fermi level of electrons in the valence band is lowered below the band edge (Fig. 33).

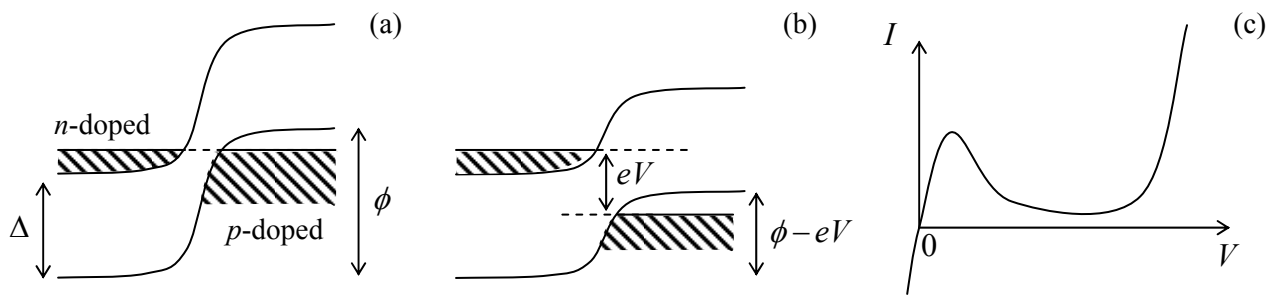


Fig. 2.33. Tunneling diode: (a) the band edge diagram of the device at zero bias; (b) the same diagram at modest positive bias $eV \sim \Delta/2$, and (c) the I - V curve (schematically). Dashed lines show the Fermi level positions.

At thermal equilibrium, and in the absence of external voltage bias, the Fermi levels self-align,⁸⁸ leading to the build-up of the *contact potential difference* ϕ/e , with ϕ somewhat larger than the energy bandgap Δ - see Fig. 33a. This potential difference creates an internal electric field that tilts the energy bands (just as the external field did in Fig. 32b), and leads to the formation of the so-called *depletion layer* in which the Fermi level located is within the energy gap and hence there are no charge carriers ready to move. In usual *p-n* junctions, this layer is broad and prevents any current at applied voltages V lower than $\sim \Delta/e$. In contrast, in a tunneling diode the depletion layer is so thin (below ~ 10 nm) that the interband tunneling is possible and provides a substantial Ohmic current at small applied voltages - see Fig. 33c.

However, at substantial positive bias, $eV \sim \Delta/2$, the conduction band become aligned with the middle of the gap in the *p*-doped electrode, and electrons cannot tunnel there. Similarly, these are no

⁸⁷ In Chapter 6, Eq. (266) will be derived using a different method based on the Golden Rule of quantum mechanics.

⁸⁸ See, e.g., SM Secs. 1.5 and 6.4.

electrons in the n -doped semiconductor to tunnel into the available states just above the Fermi level in the p -doped electrode – see Fig. 33b. As a result, current drops significantly, to grow again only when eV exceeds $\sim\Delta$ and allows the electron motion through the within each energy band. Thus the tunnel junction's I - V curve has a part with *negative differential resistance* ($dV/dI < 0$). This effect may be used for the amplification of analog signals, including self-excitation of electrical oscillators (i.e. rf signal generation),⁸⁹ and signal swing restoration in digital electronics.

2.10. Harmonic oscillator: A brute force approach

To complete our review of 1D systems, we have to consider the famous harmonic oscillator, i.e. a 1D particle moving in the quadratic-parabolic potential (111). This is just a smooth quantum well providing “soft” confinement, whose discrete spectrum we have already found in the WKB approximation – see Eq. (114). Let us try to solve the same problem exactly – not because there is anything conceptually interesting in it (there is not :-), but because of its enormous importance for applications. For that, let us write the stationary Schrödinger equation for potential (111):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{m\omega_0^2}{2} x^2 \psi = E\psi. \quad (2.268)$$

From the solution of Exercise Problem 1.5, the reader already knows⁹⁰ one of the eigenfunctions of this equation,

$$\psi_0 = C_0 \exp\left\{-\frac{m\omega_0 x^2}{2\hbar}\right\}, \quad (2.269)$$

Ground state wave-function

and the corresponding eigenenergy

$$E_0 = \frac{\hbar\omega_0}{2}. \quad (2.270)$$

Ground state energy

Expression (269) shows that the characteristic scale of wavefunction's spatial spread⁹¹ is equal to

$$x_0 \equiv \left(\frac{\hbar}{m\omega_0}\right)^{1/2}. \quad (2.271)$$

Wave-function spread scale

Due to the importance of this scale, let us give its crude estimates for several typical systems:

(i) Electrons in solids and fluids: $m \approx 10^{-30}$ kg, $\omega_0 \sim 10^{15}$ s⁻¹, giving $x_0 \sim 0.3$ nm, comparable with inter-atomic distances a . As a result, classical mechanics is not valid at all for the analysis of their motion.

(ii) Atoms in solids: $m \approx 10^{-24}$ - 10^{-26} kg, $\omega_0 \sim 10^{13}$ s⁻¹, giving $x_0 \sim 0.01$ - 0.1 nm, i.e. from $\sim$ a few percent to a few tens percent of a . Because of that, methods based classical mechanics (e.g., molecular dynamics) are approximately valid for the analysis of atomic motion, though may miss some fine effects

⁸⁹ See, e.g., CM Sec. 4.4.

⁹⁰ If not yet, I am inviting him or her to check this fact now by the direct substitution of solution (269) into the differential equation (268), simultaneously proving Eq. (270).

⁹¹ Quantitatively, as was already mentioned in Sec. 2.1, $x_0 = \sqrt{2}\delta x = \langle 2x^2 \rangle^{1/2}$.

of motion of lighter atoms – e.g., quantum tunneling of hydrogen atoms through energy barriers of the potential profile created by its neighbors.

(iii) Probe masses in modern gravity-wave detectors (Advanced LIGO, VIRGO, KAGRA, etc.):⁹² $m \sim 10^2$ kg, $\omega_0 \sim 10^2$ s⁻¹, giving $x_0 \sim 10^{-19}$ m. After several decades of development, the sensitivity of these instruments is still limited by various noise sources at the level of the order of 10^{-18} m.⁹³ Thus the prospects of observing quantum-mechanical effects in such installations do not look very realistic.

Returning to the Schrödinger equation (268), let us recast it into a dimensionless form by introducing dimensionless variable $\xi \equiv x/x_0$. This gives

$$-\frac{d^2\psi}{d\xi^2} + \xi^2\psi = \varepsilon\psi, \quad (2.272)$$

where $\varepsilon \equiv 2E/\hbar\omega_0 = E/E_0$. In this notation, the ground state wavefunction is proportional to $\exp\{-\xi^2/2\}$, so that let us look for the solutions to Eq. (272) in the form

$$\psi = C \exp\left\{-\frac{\xi^2}{2}\right\} H(\xi), \quad (2.273)$$

where $H(\xi)$ is a new function. With this substitution, Eq. (272) yields

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\varepsilon - 1)H = 0. \quad (2.274)$$

It is evident that $H = \text{const}$ and $\varepsilon = 1$ is one of its solutions, describing the eigenstate (269) with energy (270), but what are the other eigenstates and eigenvalues? This equation has been studied in detail in the mid-1800s by C. Hermite who has shown that all eigenvalues are given by equation

$$\varepsilon_n - 1 = 2n, \quad \text{with } n = 0, 1, 2, \dots, \quad (2.275)$$

so that our WKB result (114) is indeed exact for any n , and Eqs. (269) and (270) describe the ground-state of the oscillator. The eigenfunction corresponding to eigenvalue ε_n is a polynomial (now called the *Hermite polynomial*) of degree n , that may be most conveniently calculated using the following explicit formula:

$$H_n = (-1)^n \exp\{\xi^2\} \frac{d^n}{d\xi^n} \exp\{-\xi^2\}. \quad (2.276)$$

It is easy to use this formula to calculate several lowest-degree polynomials – see Fig. 34a:

$$H_0 = 1, \quad H_1 = 2\xi, \quad H_2 = 4\xi^2 - 2, \quad H_3 = 8\xi^3 - 12\xi, \quad H_4 = 16\xi^4 - 48\xi^2 + 12, \dots \quad (2.277)$$

The most important properties of the polynomials are as follows:

- (i) their “parity” (symmetry-antisymmetry) alternates with number n ,
- (ii) $H_n(\xi)$ crosses the ξ -axis exactly n times (has n zeros), and

⁹² See, e.g., <http://www.ligo.caltech.edu/>, and a recent update by T. Feder, *Phys. Today* **68**, No. 9, 20 (2015).

⁹³ According to the recent announcement by B. Abbott *et al.*, *Phys. Rev. Lett.* **116**, 061102 (2016), this sensitivity was sufficient for the first direct detection of gravitational waves emitted at a merger of two black holes.

(iii) the polynomials are mutually orthonormal in the following sense:

$$\int_{-\infty}^{+\infty} H_n(\xi) H_{n'}(\xi) \exp\{-\xi^2\} d\xi = \pi^{1/2} 2^n n! \delta_{n,n'}. \quad (2.278)$$

Using Eq. (273) to translate this result to functions $\psi_n(x)$, we get the following orthonormal eigenfunctions of the harmonic oscillator (Fig.34b):⁹⁴

$$\psi_n(x) = \frac{1}{(2^n n!)^{1/2} \pi^{1/4} x_0^{1/2}} \exp\left\{-\frac{x^2}{2x_0^2}\right\} H_n\left(\frac{x}{x_0}\right). \quad (2.279)$$

Harmonic oscillator's eigenfunctions

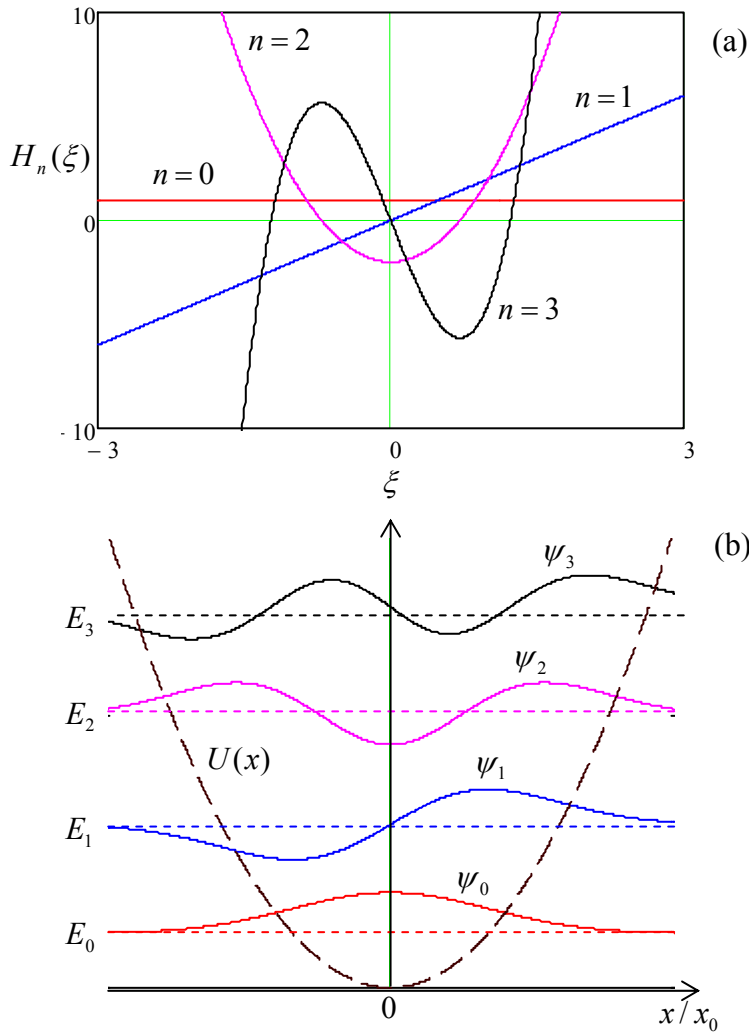


Fig. 2.34. (a) A few lowest Hermite polynomials and (b) the corresponding eigenenergies (dashed lines) and eigenfunctions (solid lines) of the harmonic oscillator. The black dashed line shows the potential profile $U(x)$, drawn on the same scale as energies E_n , so that the line crossings with the energy levels correspond to the classical turning points.

Besides its own importance, this is a typical example of eigenstates of particle confined in a soft-wall quantum well. It is very instructive to compare them with eigenstates of a the rectangular quantum well, with its ultimately-hard walls – see Eq. (1.76) and Fig. 1.7. Let us list their similar features:

⁹⁴ These stationary states of the harmonic oscillator are sometimes called its *Fock states*, to distinguish them from other fundamental solutions (such as *Glauber states*) which will be discussed in Sec. 5.5 and beyond..

(i) Wavefunctions oscillate in the classically-allowed regions with $E_n > U(x)$, while dropping exponentially beyond the boundaries of that region.

(ii) Each step up the energy level ladder increases the number of the oscillation half-waves (and hence the number of its zeros), by one.⁹⁵

Here are the major features specific for the soft confinement:

(i) The spatial spread of the wavefunction grows with n , following the gradual increase of the classically allowed region.

(ii) Correspondingly, E_n exhibits a slower growth than the $E_n \propto n^2$ law given by Eq. (1.77), because of the gradual reduction of confinement, which moderates the growth of kinetic energy.

Unfortunately, the brute-force approach to the harmonic oscillator problem, discussed above, is not too appealing intellectually. First, the proof of Eq. (276) is rather longish. More importantly, it is hard to use Eq. (279) for calculation of the so-called matrix elements of the system – as we will see in Chapter 4, virtually the only numbers important for applications. Finally, it is also almost evident that there should be some straightforward math leading to any formula as simple as Eq. (114) for E_n . Indeed, there is a much more efficient, operator-based approach to this problem; it will be described in Sec. 5.4.

2.11. Exercise problems

2.1. The initial wave packet of a free 1D particle is described by Eq. (2.20) of the lecture notes:

$$\Psi(x,0) = \int a_k e^{ikx} dk .$$

(i) Obtain a compact expression for the expectation value $\langle p \rangle$ of particle's momentum. Does $\langle p \rangle$ depend on time?

(ii) Calculate $\langle p \rangle$ for the case when function $|a_k|^2$ is symmetric with respect to some value k_0 .

2.2. Calculate the function a_k , defined by Eq. (2.20), for the wave packet with a rectangular envelope:

$$\Psi(x,0) = \begin{cases} C \exp\{ik_0 x\}, & \text{for } -a/2 \leq x \leq +a/2, \\ 0, & \text{otherwise.} \end{cases}$$

Analyze the result in the limit $k_0 a \rightarrow \infty$.

2.3. Prove Eq. (49) for the 1D propagator of a free quantum particle, starting from Eq. (48).

2.4. Express the 1D propagator, defined by Eq. (44), via eigenfunctions and eigenenergies of a particle moving in an arbitrary stationary potential $U(x)$. (For the notation simplicity, assume that the energy spectrum of the system is discrete.)

⁹⁵ In mathematics, a slightly more general statement, valid for a broader class of ordinary linear differential equations, is frequently called the *Sturm oscillation theorem*, and is a part of the *Sturm-Liouville theory* of such equations – see, e.g., Chapter 10 in the handbook by G. Arfken *et al.* recommended in MA Sec. 16.

2.5. Calculate the change of the wavefunction of a 1D particle, resulting from a short pulse of an external force, which may be approximated by the delta-function:⁹⁶

$$F(t) = P\delta(t).$$

2.6.* Analyze the effect of phase locking of Josephson oscillations on the dc current flowing through the junction, assuming that external microwave source applies a fixed sinusoidal ac voltage,

$$V(t) - \bar{V} = A \cos \omega t,$$

to a junction with sinusoidal current-phase relation (55), using Eq. (54) for time evolution of phase φ .

2.7. Calculate the transmission coefficient T as a function of particle's energy E for the rectangular potential barrier,

$$U(x) = \begin{cases} 0, & \text{for } x < -d/2, \\ U_0, & \text{for } -d/2 < x < +d/2, \\ 0, & \text{for } d/2 < x, \end{cases}$$

for the case $E > U_0$. Analyze and interpret the result, taking into account that U_0 may be either positive or negative. (In the last case, we are speaking about particle's passage over a rectangular potential well of finite depth.)

2.8. Looking at the lower (red) line in Fig. 1.7, it seems plausible that the 1D ground-state function $X(x) \propto \sin(\pi x/a)$ of the simple quantum well (1.69) may be well approximated by an inverted parabola:

$$X_{\text{trial}}(x) = Cx(a-x),$$

where C is the normalization constant, and $a \equiv a_x$ for brevity. Explore how good this approximation is.⁹⁷

2.9. Spell out the stationary wavefunctions of a harmonic oscillator in the WKB approximation, and use them to calculate the expectation values $\langle x^2 \rangle$ and $\langle x^4 \rangle$ for arbitrary state number n .

2.10.* A 1D particle of mass m is placed into the following triangular quantum well:⁹⁸

$$U(x) = \begin{cases} +\infty, & \text{for } x < 0, \\ Fx, & \text{for } x > 0, \end{cases} \quad \text{with } F > 0.$$

- (i) Calculate its energy spectrum using the WKB approximation.
- (ii) Estimate the ground state energy using the variational method.
- (iii) Calculate the three lowest energy levels, and also for the 10th level, with at least 0.1% accuracy, from the exact solution of the problem.
- (iv) Compare and discuss the results.

Hints:

⁹⁶ The constant P is called the force's *impulse*. (In higher dimensionalities, it is a vector - just as the force is.)

⁹⁷ Solving this problem is a good preparation to the use of the full *variational method* in the next two problems (and beyond).

⁹⁸ With $F = mg$, this is just the well-known *bouncing ball problem*.

- In Task (ii), try to incorporate a certain parameter λ into your trial wavefunction, and then use its adjustment to minimize the expectation value of system's Hamiltonian (mentioned in Chapter 1):

$$\langle H \rangle_{\text{trial}} \equiv \int_{-\infty}^{+\infty} \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} dx,$$

where the trial function is assumed to be properly normalized. The variational method is based on the easily provable⁹⁹ fact that this expectation value cannot be less than the genuine E_g , coinciding with it only if the trial function exactly coincides with the genuine wavefunction ψ_g of the ground state. Hence, the lower $\langle H \rangle_{\text{trial}}$ you reach, the better is your result.

- The values of the first zeros of the Airy function, necessary for Task (iii), may be found in many math handbooks, for example, in Table 10.13 of the collection edited by Abramowitz and Stegun – see MA Sec. 16(i).

2.11. For a 1D particle of mass m placed into a potential well with the following profile,

$$U(x) = ax^{2s}, \quad \text{with } a > 0 \text{ and } s > 0,$$

- (i) calculate its energy spectrum using the WKB approximation, and
- (ii) estimate the ground state energy using the variational method.

Compare the ground state energy results for parameter s equal to 1, 2, 3, and 100.

2.12. Prove Eq. (117) for the case $T_{\text{WKB}} \ll 1$, using the connection formulas (104).

2.13. Use the WKB approximation to express the expectation value of the kinetic energy of a 1D particle, confined in a soft potential well, in its n^{th} stationary state, via the derivative dE_n/dn , for $n \gg 1$.

2.14.* Use the WKB approximation to calculate the transparency T as a function of particle energy E , for the following triangular potential barrier:

$$U(x) = \begin{cases} 0, & \text{for } x < 0, \\ U_0 - Fx, & \text{for } x > 0, \end{cases}$$

with $F, U_0 > 0$.

Hint: Be careful treating the sharp potential step at $x = 0$.

2.15.* Prove that the symmetry of the scattering matrix elements describing an arbitrary time-independent scatterer allows its representation in the form (136a), with the additional restriction (136b).

2.16. Prove the universal relations between elements of the transfer matrix T of a stationary (but otherwise arbitrary) 1D scatterer, which were mentioned in Sec. 5.

2.17. For a deep and narrow 1D quantum well, modeled by a delta-function,

$$U(x) = -w\delta(x), \quad \text{with } w > 0, \quad (*)$$

⁹⁹ See, e.g., Sec. 8.2 below.

find the localized eigenfunction(s) ψ_n (with $|\psi_n(x)| \rightarrow 0$ at $|x| \rightarrow \infty$), and the corresponding value(s) E_n .

2.18. A 1D particle was localized in the delta-functional well, with $U(x) = -\mathcal{W}\delta(x)$, such as the one analyzed in the previous problem. Then (say, at $t = 0$) the well's bottom is suddenly lifted, so that the particle becomes free to move. Calculate the probability density, $w(k)$ to find the particle in a state with wave number k at $t > 0$, and the final total energy of the system.

2.19. Calculate the lifetime of the metastable localized state of a 1D particle in the potential

$$U(x) = -\mathcal{W}\delta(x) - Fx, \quad \text{with } \mathcal{W} > 0,$$

using the WKB approximation. Formulate the condition of validity of the result.

2.20. Analyze the localized eigenfunction(s) and the characteristic equation(s) for eigenenergies of a 1D particle in the following two-well potential

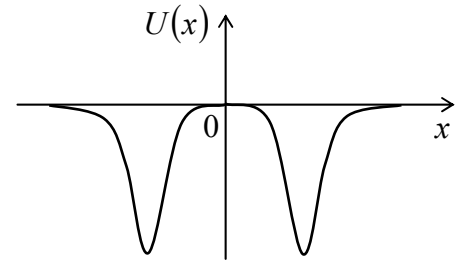
$$U(x) = -\mathcal{W} \left[\delta\left(x - \frac{a}{2}\right) + \delta\left(x + \frac{a}{2}\right) \right], \quad \text{with } \mathcal{W} > 0.$$

Explore asymptotic behaviors of the eigenenergies in the limits of very strong and very weak potential, and find the number of localized states as a function of distance a .

2.21.* Consider a symmetric system of two quantum wells of the type shown in Fig. 23, but with $U(0) = U(\pm\infty) = 0$ – see Fig. on the right. What is the sign of well interaction force due to a quantum particle of mass m , shared by them, for the cases when the particle is in:

- (i) a symmetric eigenstate, with $\psi_s(-x) = \psi_s(x)$?
- (ii) an asymmetric eigenstate, with $\psi_a(-x) = -\psi_a(x)$?

Use a different approach to confirm your result for the particular case of delta-functional wells, considered in the previous problem.



2.22. Derive and analyze the characteristic equation for eigenvalues for a particle in a rectangular well of a finite depth:

$$U(x) = \begin{cases} -U_0, & \text{for } |x| \leq a/2, \\ 0, & \text{otherwise.} \end{cases}$$

In particular, calculate the number of localized states as a function of well's width a , and explore the limit $U_0 \ll \hbar^2/2ma^2$.

2.23. Calculate energy E of the localized state in a quantum well of an arbitrary shape $U(x)$, provided that its width a is finite, and the average depth is very small:

$$|\bar{U}| \ll \frac{\hbar^2}{2ma^2}, \quad \text{where } \bar{U} \equiv \frac{1}{a} \int_{\text{well}} U(x) dx.$$

2.24.* A particle of mass m is moving in a field with the following potential:

$$U(x) = U_0(x) + \mathcal{W}\delta(x),$$

where $U_0(x)$ describes a smooth, symmetric function with $U_0(0) = 0$, growing monotonically at $x \rightarrow \pm\infty$.

- (i) Use the WKB approximation to derive the characteristic equation for the energy spectrum;
- (ii) semi-quantitatively describe the spectrum structure evolution at the increase of $|\mathcal{W}|$, for both signs of this parameter, and make the results more specific for the quadratic potential

$$U_0(x) = \frac{m}{2} \omega_0^2 x^2.$$

2.25. Prove Eq. (191), starting from Eq. (190).

2.26. For the problem explored in the beginning of Sec. 7, i.e. 1D particle's motion in a delta-functional periodic potential shown in Fig. 24,

$$U(x) = \mathcal{W} \sum_{j=-\infty}^{+\infty} \delta(x - ja), \quad \text{with } \mathcal{W} > 0,$$

(where j are integers), write explicit expressions for its eigenfunctions:

- (i) at the bottom, and
- (ii) at the top

of the lowest energy band. Sketch both eigenfunctions.

2.27.* A 1D particle of mass m moves in an infinite periodic system of very narrow and deep quantum wells that may be described by delta-functions:

$$U(x) = \mathcal{W} \sum_{j=-\infty}^{+\infty} \delta(x - ja), \quad \text{with } \mathcal{W} < 0.$$

(i) Sketch the energy band structure of the system for relatively small and relatively large values of the quantum well's "area" $|\mathcal{W}|$, and

(ii) calculate explicitly the ground state energy of the system in the limits of very small and very large $|\mathcal{W}|$.

2.28.* For the system discussed in the previous problem, write explicit expressions for the eigenfunctions of the system, corresponding to:

- (i) the bottom points of the lowest energy band, and
- (ii) the top points of that band, and
- (iii) the lowest points of each higher energy band,

and sketch the functions.

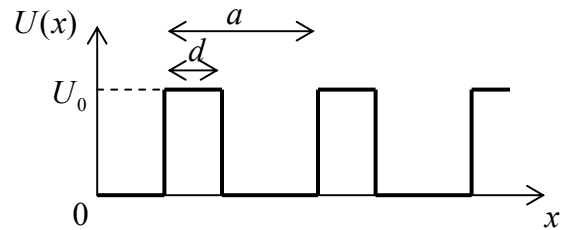
2.29.* The 1D “crystal”, analyzed in the last two problems, now extends along only to $x > 0$, while bordering a flat potential step at $x = 0$.¹⁰⁰

$$U(x) = \begin{cases} w \sum_{j=1}^{+\infty} \delta(x - ja), & \text{with } w < 0, & \text{for } x > 0, \\ U_0 > 0, & & \text{for } x < 0. \end{cases}$$

Prove that the system can have a set of so-called *Tamm states*, localized near the “surface” $x = 0$, and calculate their energies in the limit when U_0 is very large but finite. (Quantify this condition.)

2.30. Calculate the whole transfer matrix of the rectangular tunnel barrier, specified by Eq. (76), for particle energies both below and above U_0 .

2.31. Use results of the previous problem to calculate the transfer matrix of one period of the periodic Kronig-Penney potential shown in Fig. 30b (reproduced in Fig. on the right).



2.32. Using results of the previous problem, derive the characteristic equations for particle’s motion in the periodic Kronig-Penney potential, for both $E < U_0$ and $E > U_0$. Try to bring the equations to a form similar to that obtained in Sec. 5 for the delta-functional barriers – see Eq. (166). Use the equations to formulate the conditions of applicability of the tight-binding and weak-potential approximations, in terms of parameters U_0 , d , and a of the potential profile, and particle’s mass m and energy E .

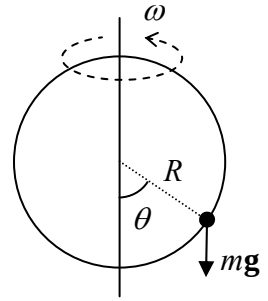
2.33.* For the Kronig-Penney potential, use the tight binding approximation to calculate the widths of the allowed energy bands. Compare the results with those of the previous problem (in the corresponding limit).

2.34.* For the same Kronig-Penney potential, use the weak potential limit formulas to calculate the energy gap widths. Again, compare the results with those of Problem 30, in the corresponding limit.

2.35. 1D periodic chains of atoms may exhibit what is called the so-called *Peierls instability*, leading to the *Peierls transition* to phase in which atoms are slightly displaced by $\Delta x_j = (-1)^j \Delta x$, with $\Delta x \ll a$. These displacements lead to the alternation of coupling amplitudes δ_n (see Eq. (204)) between some values δ_n^+ and δ_n^- . Use the tight-binding approximation to calculate the resulting change of the n^{th} energy band, and discuss the result.

¹⁰⁰ In applications to electrons in solid-state crystals, the delta-functional quantum wells model the attractive potential of atomic nuclei, while U_0 represents the *workfunction*, i.e. the energy necessary for the extraction of an electron from the crystal to the free space – see, e.g., EM Sec. 2.6 and SM Sec. 6.4.

2.36. Assuming the quantum effects to be small, calculate the lower part of the energy spectrum of the following system: a small bead of mass m , free to move without friction along a ring of radius R that is rotated about its vertical diameter with a constant angular velocity ω - see Fig. on the right.¹⁰¹ Formulate a quantitative condition of validity of your results.



2.37. A 1D harmonic oscillator (with mass m and frequency ω_0) had been in its ground state; then an additional force F was suddenly applied (and retained constant in time). Find the probability of the oscillator staying in its ground state.

2.38. A 1D particle of mass m has been placed into a quadratic potential well (111),

$$U(x) = \frac{m\omega_0^2}{2}x^2,$$

and allowed to relax into the ground state. harmonic oscillator had been in its ground state. At $t = 0$, the well starts to be moved with velocity v , without changing its profile, so that at $t \geq 0$ the above formula for U is valid with the replacement $x \rightarrow x' \equiv x - vt$. Calculate the probability for the system to still be in the ground state at $t > 0$.

2.39. A 1D particle is placed into the following potential well:

$$U(x) = \begin{cases} +\infty, & \text{for } x < 0, \\ m\omega_0^2 x^2 / 2, & \text{for } x \geq 0. \end{cases}$$

(i) Find its eigenstates and eigenenergies.

(ii) This system had been let to relax into its ground state, and then the potential wall at $x < 0$ was rapidly removed, so that the system was instantly turned into the usual harmonic oscillator (with the same m and ω_0). Find the probability for the oscillator to be in its ground state.

2.40. Prove the following formula for the propagator of the 1D harmonic oscillator:

$$G(x, t; x_0, t_0) = \left(\frac{m\omega_0}{2\pi i \hbar \sin[\omega_0(t - t_0)]} \right)^{1/2} \exp \left\{ \frac{im\omega_0}{2\hbar \sin[\omega_0(t - t_0)]} \left[(x^2 + x_0^2) \cos[\omega_0(t - t_0)] - 2xx_0 \right] \right\}.$$

Discuss the relation between this formula and the propagator of a free 1D particle.

2.41. Use the variational method to estimate the ground state energy E_g of the following confined 1D systems:

(i) a harmonic oscillator, with $U(x) = m\omega_0^2 x^2 / 2$, and

(ii) a particle in the following potential well: $U(x) = -U_0 \exp\{-\alpha^2 x^2\}$, and $U_0 > 0$.

¹⁰¹ This system was used as the analytical mechanics “testbed problem” in the CM part of this series, and the reader is welcome to use any relations derived there - but remember that they pertain to the classical mechanics domain!

In the latter case, get explicit results in the limits of small and large U_0 , and give their interpretation.

2.42. * Use the WKB approximation to calculate the lifetime of the metastable ground state of a 1D particle of mass m in the “pocket” of the potential profile

$$U(x) = \frac{m\omega_0^2}{2}x^2 - \alpha x^3.$$

Contemplate the significance of this problem.

2.43. In the context of the Sturm oscillation theorem mentioned in Sec. 10, prove that the number of zeros of stationary wavefunctions of a particle, confined in an arbitrary potential well, always increases with energy.

Hint: You may like to use the suitably modified Eq. (189).

Chapter 3. Higher Dimensionality Effects

The coverage of multi-dimensional problems of wave mechanics in this course is minimal: it is limited to a few phenomena (such as the AB effect and Landau levels) that cannot take place in one dimension due to topological reasons, and a few key 3D problems (such as the Born approximation in scattering theory and the Bohr atom) whose solutions are necessary for numerous applications.

3.1. Quantum interference and the AB effect

In the past two chapters, we have already discussed some effects of the de Broglie wave interference. For example, standing waves inside a quantum well, or even on the top of a tunnel barrier, may be considered as a result of the incident and reflected waves. However, there are some remarkable new effects made possible by the spatial separation of such traveling waves, and such separation requires a higher (either 2D or 3D) dimensionality. A good example of such separation is provided by the Young-type experiment (Fig. 1) in which particles are passed through two narrow holes (or slits) in an otherwise opaque partition.

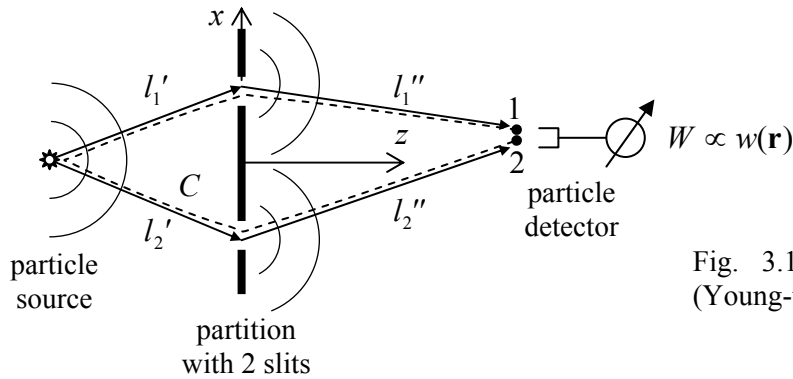


Fig. 3.1. Scheme of the “two-slit” (Young-type) interference experiment.

If the particles emitted by the source do not interact (which is always true if the emission rate is sufficiently low), the average rate of particle counting by the detector is proportional to the probability density $w(\mathbf{r}, t) = \Psi(\mathbf{r}, t) \Psi^*(\mathbf{r}, t)$ to find a single particle at the detector's location $\mathbf{r}$, where $\Psi(\mathbf{r}, t)$ is the solution of the single-particle Schrödinger equation (1.25). Let us describe this experiment for the case when the particles may be represented by monochromatic waves of energy E (e.g., very $\mathbf{r}$ -long wave packets), so that the wavefunction may be taken in the form given by Eqs. (1.56) and (1.61): $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\{-iEt/\hbar\}$. In this case, in the free-space parts of the system, $\psi(\mathbf{r})$ satisfies the stationary Schrödinger equation (1.60) with Hamiltonian (1.27a):

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi. \quad (3.1a)$$

With the standard definition $k \equiv (2mE)^{1/2}/\hbar$, it may be rewritten as the 3D Helmholtz equation

$$\nabla^2 \psi + k^2 \psi = 0 \quad (3.1b)$$

– an evident 3D generalization of Eqs. (1.75) or (2.81).

The opaque parts of the partition may be well described as classically forbidden regions, so if their size scale a is much larger than the wavefunction penetration depth δ (2.67), we can use on their surface S the same boundary conditions as for the quantum barrier of infinite height:

$$\psi|_S = 0. \quad (3.2)$$

Equations (1) and (2) formulate the standard boundary problem of the theory of propagation of scalar waves of any nature. For an arbitrary geometry, such problem does not have a simple analytical solution. However, for a conceptual discussion of interference we use certain natural assumptions that will allow us to find its particular, approximate solution.

First, let us discuss wave emission, into free space, by a small-size source located at the origin. Naturally, the emitted wave should be spherically-symmetric: $\psi(\mathbf{r}) = \psi(r)$. Using the well-known expression for the Laplace operator in spherical coordinates,¹ we then reduce Eq. (1) to an ordinary differential equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) + k^2 \psi = 0. \quad (3.3)$$

Let us introduce a new function, $f(r) = r\psi(r)$. Plugging the reciprocal relation $\psi = f/r$ into Eq. (3), we see that it is reduced to the 1D wave equation,

$$\frac{d^2 f}{dr^2} + k^2 f = 0, \quad (3.4)$$

whose solutions were discussed in detail in Sec. 2.2. For a fixed k , the general solution of Eq. (4) is

$$f = f_+ e^{ikr} + f_- e^{-ikr} \quad (3.5)$$

so that the full wavefunction

$$\psi(\mathbf{r}) = \frac{f_+}{r} e^{ikr} + \frac{f_-}{r} e^{-ikr}, \quad \text{i.e. } \Psi(\mathbf{r}, t) = \frac{f_+}{r} e^{i(kr - \omega t)} + \frac{f_-}{r} e^{-i(kr + \omega t)}, \quad \text{with } \omega \equiv \frac{E}{\hbar} = \frac{\hbar k^2}{2m}. \quad (3.6)$$

If the source is located at point $\mathbf{r}' \neq 0$, the obvious generalization of Eq. (6)

$$\Psi(\mathbf{r}, t) = \frac{f_+}{R} e^{i(kR - \omega t)} + \frac{f_-}{R} e^{-i(kR + \omega t)}, \quad \text{with } R \equiv |\mathbf{R}|, \quad \mathbf{R} \equiv \mathbf{r} - \mathbf{r}'. \quad (3.7)$$

The first term of this solution describes a spherically-symmetric wave propagating from the source outward, while the second one, a wave converging onto the source point $\mathbf{r}'$ from large distances. Though the latter solution is possible at some very special circumstances (say, when the outgoing wave is reflected back from a spherical shell), for our problem, only the outgoing waves are relevant, so that we may keep only the first term (proportional to f_+) in Eq. (7). Note that factor R is the denominator (that was absent in 1D geometry) has a simple physical sense: it provides the independence of the full probability current $I = 4\pi R^2 j(R)$, with $j(R) \propto k \Psi \Psi^* \propto 1/R^2$, of the distance R between the observation point and the source.

¹ See, e.g., MA Eq. (10.9).

Now let us assume that the partition's geometry is not too complicated – for example, it is planar as shown in Fig. 1, and consider the region of the particle detector location far behind the partition (at $z \gg 1/k$), and at a relatively small angle to it: $|x| \ll z$. Then it should be physically clear that the spherical waves (7) emitted by each point inside the slit cannot be perturbed too much by the opaque parts of the partition, and their only role is the restriction of the set of such emitting points by the area of the slits. Hence, an approximate solution of the boundary problem is given by the following *Huygens principle*: the wave behind the partition looks as if it was the sum of contributions (7) of point sources located in the slits, with each source's strength f_+ proportional to the amplitude of the wave arriving at this pseudo-source from the real source – see Fig. 1. This principle finds its confirmation in strict wave theory, which shows² that with our assumptions, the solution of the boundary problem (1)-(2) may be presented as the following *Kirchhoff integral*:

Kirchhoff
integral

$$\psi(\mathbf{r}) = c \int_{\text{slits}} \frac{\psi(\mathbf{r}')}{R} e^{ikR} d^2r', \quad \text{with } c = \frac{k}{2\pi i}. \quad (3.8)$$

If the source is also far from the partition, its wave front is almost parallel to the slit plane, and the slits are not too broad, we can take $\psi(\mathbf{r}')$ constant ($\psi_{1,2}$) at each slit, so that Eq. (8) is reduced to

$$\psi(\mathbf{r}) = a''_1 \exp\{ikl''_1\} + a''_2 \exp\{ikl''_2\}, \quad \text{with } a''_{1,2} = \frac{cA_{1,2}}{l''_{1,2}} \psi_{1,2}, \quad (3.9)$$

where $A_{1,2}$ are the slit areas. The wavefunctions on the slits be calculated approximately³ by applying the same Eq. (7) to the space *before* the slits: $\psi_{1,2} \approx (f_+/l'_{1,2}) \exp\{ikl'_{1,2}\}$. As a result, Eq. (9) may be rewritten as

Wave-
function
superposition

$$\psi(\mathbf{r}) = a_1 \exp\{ikl_1\} + a_2 \exp\{ikl_2\}, \quad \text{with } l_{1,2} \equiv l'_{1,2} + l''_{1,2}, \quad a_{1,2} \equiv \frac{c f_+ A_{1,2}}{l'_{1,2} l''_{1,2}}. \quad (3.10)$$

(As Fig. 1 shows, each of $l_{1,2}$ is the length of the full classical path of the particle from the source, through the corresponding slit, and further to the observation point $\mathbf{r}$ – see Fig. 1).

According to Eq. (10), the resulting rate of particle counting is proportional to

$$w(\mathbf{r}) = \psi(\mathbf{r})\psi^*(\mathbf{r}) = |a_1|^2 + |a_2|^2 + 2|a_1 a_2| \cos \varphi_{12}, \quad (3.11)$$

where

$$\varphi_{12} \equiv k(l_2 - l_1) \quad (3.12)$$

is the difference of the total wave phase accumulations along each of two alternative trajectories. The last expression may be evidently generalized as

² For a proof of Eq. (8), see, e.g., EM Sec. 8.5.

³ A possible (and reasonable) concern about the application of Eq. (7) to the field in the slits is that it ignores the effect of opaque parts of the partition. However, as we know from Chapter 2, the main role of the classically forbidden region is providing the reflection of the incident wave towards its source (i.e. to the left in Fig. 1). As a result, the contribution of this reflection to the field inside the slits is insignificant is $A_{1,2} \gg \lambda^2$, and even in the opposite case provides just some rescaling of the amplitudes $a_{1,2}$, which is unimportant for our conceptual discussion.

$$\varphi_{12} = \oint_C \mathbf{k} \cdot d\mathbf{r}, \quad (3.13)$$

with integration along the virtually closed contour C (see the dashed line in Fig. 1), i.e. from point 1, in the positive (i.e. counterclockwise) direction to point 2. (From our experience with the 1D WKB approximation we may expect such generalization to be valid even if k changes, sufficiently slowly, along the paths.)

Our result (11) shows that the counting rate oscillates as a function of the difference $(l_2 - l_1)$ that in turn changes with detector's position, giving the famous interference pattern, with the amplitude proportional to the product $|a_1 a_2|$, and hence vanishing if any of the slits is closed. For a wave theory, this is a well-known result,⁴ but for particle physics, it was (and still is :-) rather shocking. Indeed, our analysis pertains to a very low particle emission/detection rate, so that there is no other way to interpret it rather than resulting from particle's interference *with itself*, or rather the interference of its wavefunction parts passing through each of two slits.

Let us now discuss a very interesting effect of magnetic field on the quantum interference. In order to make the discussion simpler, let us consider an alternative version of the two-slit experiment, in which each of alternative path is fixed to a narrow channel using a partial confinement – see Fig. 2. (In this arrangement, moving the particle detector without changing channels' geometry, and hence local values of k may be more problematic in experimental practice, so let us think about its position $\mathbf{r}$ fixed.)

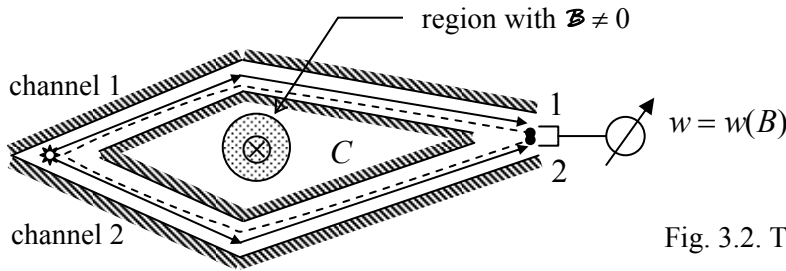


Fig. 3.2. The AB effect.

In this case, because of the effect of the walls providing the path confinement, we cannot use expressions (10) for amplitudes $a_{1,2}$. However, from the discussions in Sec. 1.6 and Sec. 2.2, it should be clear that the first of expressions (10) remains valid, though may be with a value of k specific for each channel.

The benefit of this geometry is that we can now apply magnetic field $\mathcal{B}$, perpendicular to the plane of particle motion, that would pierce contour C , but would not touch the particle propagation channels. In classical physics, magnetic field's effect on a particle with electric charge q is described by the *Lorentz force*⁵

$$\mathbf{F}_{\mathcal{B}} = q\mathbf{v} \times \mathcal{B}, \quad (3.14)$$

⁴ See, e.g., a detailed discussion in EM Sec. 8.4.

⁵ See, e.g., Sec. 5.1. Note that Eq. (14), as well as all other formulas of this course, are in the SI units; in Gaussian units, all terms which include either $\mathcal{B}$ or $\mathbf{A}$ should be divided by c , the speed of light in free space.

where $\mathcal{B}$ is the field value at the point of its particle's location, so that for the experiment shown in Fig. 2, $\mathbf{F}_{\mathcal{B}} = 0$, and the field would not affect the particle motion at all. In quantum mechanics, this is not so, and the field does affect the probability density w , even if $\mathcal{B} = 0$ in all points where the wavefunction $\psi(\mathbf{r})$ is not equal to zero.

In order to describe this surprising effect, let us first develop a general framework for account of effects of electromagnetic fields on a quantum particle, which will also give us some important by-product results. In order to do that, we need to calculate the Hamiltonian operator of a charged particle in the field. For an electrostatic field, this hardly present any problem. Indeed, from classical electrodynamics we know that such field may be presented as a gradient of its electrostatic potential ϕ ,

$$\mathcal{E} = -\nabla\phi(\mathbf{r}), \quad (3.15)$$

so that the force exerted by the field on a particle with electric charge q ,

$$\mathbf{F}_{\mathcal{E}} = q\mathcal{E}, \quad (3.16)$$

may be described by adding the potential energy of the field,

$$U(\mathbf{r}) = q\phi(\mathbf{r}), \quad (3.17)$$

to other (possible) components of the full potential energy of the particle. As we have already discussed, such a function of coordinates may be included to the Hamiltonian operator just by adding it to the kinetic energy operator (1.27).

However, magnetic field's effect is peculiar: since its Lorentz force (14) cannot do any work on the particle:

$$dW_{\mathcal{B}} \equiv \mathbf{F}_{\mathcal{B}} \cdot d\mathbf{r} = \mathbf{F}_{\mathcal{B}} \cdot \mathbf{v}dt = q(\mathbf{v} \times \mathcal{B}) \cdot \mathbf{v}dt = 0, \quad (3.18)$$

the field cannot be presented by any potential energy, so it may not be immediately clear how to account for it in the Hamiltonian. Help comes from the analytical-mechanics approach to classical electrodynamics:⁶ in the nonrelativistic limit, the Hamiltonian function of a particle in electromagnetic field looks superficially like that in electrostatic field only:

$$H = \frac{mv^2}{2} + U = \frac{p^2}{2m} + q\phi; \quad (3.19)$$

however, the momentum $\mathbf{p} \equiv m\mathbf{v}$ that participates in this expression is now the difference

$$\mathbf{p} = \mathbf{P} - q\mathbf{A}. \quad (3.20)$$

Here $\mathbf{A}$ is the vector-potential, defined by the well-known relations for the electric and magnetic field:⁷

$$\mathcal{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathcal{B} = \nabla \times \mathbf{A}, \quad (3.21)$$

while $\mathbf{P}$ is the *canonical momentum* whose Cartesian components may be calculated (in classics) from the Lagrangian function,⁸ using the standard formula of analytical mechanics,

⁶ See, e.g., EM Sec. 9.7.

⁷ See, e.g., EM Sec. 6.7, in particular Eqs. (6.106).

⁸ Just for reader's reference, the classical Lagrangian corresponding to Hamiltonian (19) is

$$P_j \equiv \frac{\partial L}{\partial v_j}. \quad (3.22)$$

To emphasize the difference between the two momenta, $\mathbf{p} = m\mathbf{v}$ is frequently called the *kinematic momentum* (or “ $m\mathbf{v}$ -momentum”). The distinction between $\mathbf{p}$ and $\mathbf{P} = \mathbf{p} + q\mathbf{A}$ becomes even more clear if we notice that vector-potential is not *gauge-invariant*: according to the second of Eqs. (21), at the so-called *gauge transformation*

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi, \quad (3.23)$$

with an arbitrary single-valued scalar *gauge function* $\chi = \chi(\mathbf{r}, t)$, the magnetic field does not change. Moreover, according to the first of Eqs. (21), if we make the simultaneous replacement

$$\phi \rightarrow \phi - \frac{\partial\chi}{\partial t}, \quad (3.24)$$

the gauge transformation does not affect the electric field either. With that, the gauge function does not change the classical particle’s equation of motion, and hence the velocity $\mathbf{v}$ and momentum $\mathbf{p}$. Hence, the kinematic momentum is gauge-invariant, while $\mathbf{P}$ is not, because it changes by $q\nabla\chi$.

Now the standard way of transfer to quantum mechanics is to treat the canonical rather than kinematic momentum according to correspondence postulate discussed in Sec. 1.2. This means that in the coordinate representation, the operator of this variable is given by Eq. (1.26):⁹

$$\hat{\mathbf{P}} = -i\hbar\nabla. \quad (3.25)$$

Canonical
momentum
operator

Hence the Hamiltonian operator corresponding to the classical function (19) is

$$\hat{H} = \frac{1}{2m}(-i\hbar\nabla - q\mathbf{A})^2 + q\phi = -\frac{\hbar^2}{2m}\left(\nabla - \frac{iq}{\hbar}\mathbf{A}\right)^2 + q\phi, \quad (3.26)$$

so that the Schrödinger equation of a particle moving in electromagnetic field (but otherwise free) is

$$-\frac{\hbar^2}{2m}\left(\nabla - \frac{iq}{\hbar}\mathbf{A}\right)^2\psi + q\phi\psi = E\psi, \quad (3.27)$$

Charged
particle
in EM field

We may now repeat all the calculations of Sec. 1.4 for the case $\mathbf{A} \neq 0$, and readily get the following generalized expression for the probability current density:

$$\mathbf{j} = \frac{\hbar}{2im}\left[\psi^*\left(\nabla - \frac{iq}{\hbar}\mathbf{A}\right)\psi - \text{c.c.}\right] = \frac{1}{2m}[\psi^*\hat{\mathbf{P}}\psi - \text{c.c.}] = \frac{\hbar}{m}|\psi|^2\left(\nabla\phi - \frac{q}{\hbar}\mathbf{A}\right). \quad (3.28)$$

$$L = \frac{mv^2}{2} + q\mathbf{v} \cdot \mathbf{A} - q\phi$$

- see EM Sec. 9.7. Note that this function includes $\mathbf{A}$ within a term that cannot be interpreted as either the purely kinetic energy (as the first term) or the purely potential energy (as the last term with the minus sign).

⁹ The validity of this choice is clear from the fact that if the *kinetic* momentum was described by this differential operator, the Hamiltonian operator corresponding to the classical Hamiltonian function (19) would not include the magnetic field at all, and hence solutions of the corresponding Schrödinger equation could not satisfy the correspondence principle.

We see that the current density is gauge-invariant (as required for any observable) only if the wavefunction's phase φ changes as

$$\varphi \rightarrow \varphi + \frac{q}{\hbar} \chi. \quad (3.29)$$

This may be a point of concern: since the quantum interference is described by the spatial dependence of phase φ , can the observed interference pattern depend on the gauge function choice (which would not make sense)? Fortunately, this is not true, because the spatial phase *difference* between two interfering paths, participating in Eq. (11), is gauge-transformed as

$$\varphi_{12} \rightarrow \varphi_{12} + \frac{q}{\hbar} (\chi_2 - \chi_1). \quad (3.30)$$

But χ has to be a single-valued function of coordinates, hence in the limit when points 1 and 2 coincide, $\chi_1 = \chi_2$, so that $\Delta\varphi$ (and hence the interference pattern) is gauge-invariant.

However, the difference φ *may be* affected by the magnetic field, even if it is localized outside the channels in which the particle propagates. Indeed, in this case the field cannot not affect particle's velocity and current density $\mathbf{j}$:

$$\mathbf{j}(\mathbf{r})|_{\mathcal{B} \neq 0} = \mathbf{j}(\mathbf{r})|_{\mathcal{B} = 0}, \quad (3.31)$$

so that the last form of Eq. (28) yields

$$\nabla\varphi(\mathbf{r})|_{\mathcal{B} \neq 0} = \nabla\varphi(\mathbf{r})|_{\mathcal{B} = 0} + \frac{q}{\hbar} \mathbf{A}. \quad (3.32)$$

Integrating this equation along contour C (Fig. 2), for the phase difference between points 1 and 2 we get

$$\varphi_{12}|_{\mathcal{B} \neq 0} = \varphi_{12}|_{\mathcal{B} = 0} + \frac{q}{\hbar} \oint_C \mathbf{A} \cdot d\mathbf{r}, \quad (3.33)$$

where the integral should be taken along the same virtually closed contour C as before (in Fig. 2, from point 1, counterclockwise along the dashed line to point 2). But from the classical electrodynamics we know¹⁰ that as points 1 and 2 are overlapped, i.e. contour C becomes closed, the last integral is just the magnetic flux $\Phi \equiv \int \mathcal{B}_n d^2r$ through any smooth surface limited by contour C , so that Eq. (33) may be presented as

$$\varphi_{12}|_{\mathcal{B} \neq 0} = \varphi_{12}|_{\mathcal{B} = 0} + \frac{q}{\hbar} \Phi. \quad (3.34a)$$

In terms of the interference pattern, this means a shift of interference fringes, proportional to the magnetic flux (Fig. 3). This phenomenon is usually called the “Aharonov-Bohm” (or just the *AB effect*).¹¹ For particles with a single elementary charge, $q = \pm e$, this result is frequently presented as

¹⁰ See, e.g., EM Sec. 5.3.

¹¹ I personally prefer the latter, less personable name, because the effect had been actually predicted by W. Ehrenberg and R. Siday in 1949, before it was rediscovered by Y Aharonov and D. Bohm in 1959. To be fair to Aharonov and Bohm, it was their work that triggered a wave of interest to the phenomenon, resulting in its first

$$\varphi_{12}|_{\mathcal{B} \neq 0} = \varphi_{12}|_{\mathcal{B}=0} \pm 2\pi \frac{\Phi}{\Phi_0'}, \quad (3.34b)$$

where the fundamental constant $\Phi_0' \equiv 2\pi\hbar/e = h/e \approx 4.14 \times 10^{-15}$ Wb has the meaning of flux necessary to change φ_{12} by 2π , i.e. shift the interference pattern (11) by one period, and is called the *normal magnetic flux quantum*, because of the reasons we will soon discuss.

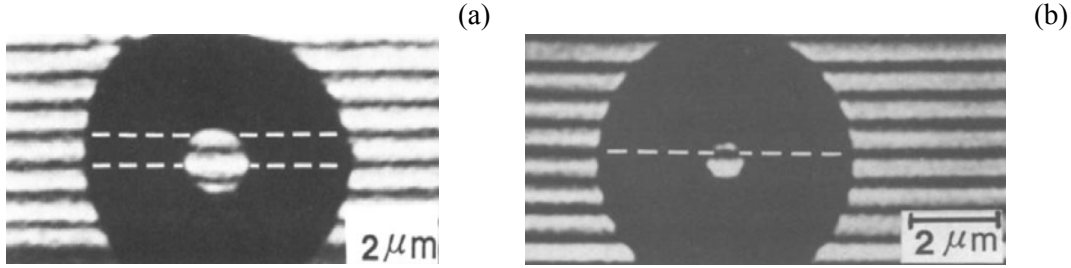


Fig. 3.3. Typical results of a two-paths interference experiment by A. Tonomura *et al.*, *Phys. Rev. Lett.* **56**, 792 (1986), showing the AB effect for electrons well shielded from the applied magnetic field. In this particular experimental geometry, the AB effect produces a relative shift of the interference patterns inside and outside the dark ring. (a) $\Phi = \Phi_0'/2$, (b) $\Phi = \Phi_0'$. © 1986 APS.

The AB effect may be “almost explained” classically, in terms of Faraday’s electromagnetic induction. Indeed, a change $\Delta\Phi$ of magnetic flux in time causes a vortex-like electric field $\Delta\mathcal{E}$ around it. That field is *not* restricted to the magnetic field’s location, i.e. may reach particle’s trajectories. The field’s magnitude (or rather of its integral along contour C) may be readily calculated by integration of the first of Eqs. (21):

$$\Delta V \equiv \oint_C \Delta\mathcal{E} \cdot d\mathbf{r} = -\frac{d\Phi}{dt}, \quad (3.35)$$

I hope that in this expression the reader readily recognizes the integral (“undergraduate”) form of Faraday’s induction law. Now let us assume that the variable separation described in Sec. 1.5 may be applied to the end points 1 and 2 of particle’s alternative trajectories as two independent systems,¹² and that the magnetic flux’ change by certain amount $\Delta\Phi$ does not change the spatial parts ψ_f of wavefunctions of these systems. Then change (35) leads to the change of potential energy difference $\Delta U = q\Delta V$ between the two points, and repeating the arguments that were used in Sec. 2.3 at the discussion of the Josephson effect, we may rewrite Eq. (2.53) as

$$\frac{d\varphi_{12}}{dt} = -\frac{\Delta U}{\hbar} = -\frac{q}{\hbar} \Delta V = \frac{q}{\hbar} \frac{d\Phi}{dt}. \quad (3.36)$$

Integrating this relation over the time of magnetic field’s change, we get

experimental observation by R. Chambers in 1960 and several other groups soon after that. Later, the experiments were improved, using ferromagnetic cores and/or superconducting shielding to provide better separation between the electron trajectories and the applied magnetic field,— see in the work whose results are shown in Fig. 3.

¹² This assumption may seem a bit of a stretch, but the resulting relation (37) may be indeed proven for a rather realistic model, though that would take more time and space that I can afford.

$$\Delta\varphi_{12} = \frac{q}{\hbar} \Delta\Phi, \quad (3.37)$$

- superficially, the same result as given by Eq. (34).

However, this interpretation of the AB effect is limited. Indeed, it requires the particle to be in the system (on the way from the source to the detector) during the flux change, i.e. when the induced electric field $\mathcal{E}$ may affect its dynamics. On the contrary, Eq. (34) predicts that the interference pattern would shift even if the field change has been made when there is no particle in the system, and hence field $\mathcal{E}$ could not be felt by it. Experiment confirms the latter conclusion. Hence, there is *something* in the space where a particle propagates (i.e., outside of the magnetic field region), which transfers information about even the static magnetic field to the particle. The standard interpretation of this surprising fact is as follows: the vector-potential $\mathbf{A}$ is not just a convenient mathematical tool, but a physical reality (just as its electric counterpart ϕ), despite the large freedom of choice we have in prescribing specific spatial and temporal dependences of these potentials without affecting any observable – see Eqs. (23)-(24).

Let me briefly discuss the very interesting form the AB effect takes in superconductivity. In this case, our results require two changes. The first one is simple: since superconductivity may be interpreted as the Bose-Einstein condensate of Cooper pairs with electric charge $q = 2e$, Φ_0 has to be replaced by the so-called *superconducting flux quantum*¹³

$$\Phi_0 \equiv \frac{\pi\hbar}{e} \approx 2.07 \times 10^{-15} \text{ Wb} = 2.07 \times 10^{-7} \text{ Gs} \cdot \text{cm}^2. \quad (3.38)$$

Super-
conducting
flux
quantum

Second, since the pairs are Bose particles and are all condensed in the same quantum state, described by the same wavefunction, the total electric current density, proportional to the probability current density j , may be extremely large – in real superconducting materials, up to $\sim 10^{12} \text{ A/m}^2$. In these conditions, one cannot neglect the contribution of that current into the magnetic field and hence its flux Φ , which (according to the Lenz rule of the Faraday induction law) tries to compensate changes in external flux. In order to see possible results of this contribution, let us consider a closed superconducting loop (Fig. 4).

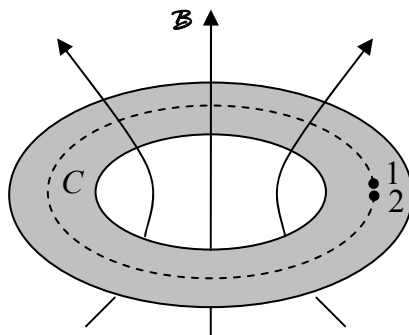


Fig. 3.4. Flux quantization in a superconducting loop.

Due to the Meissner effect (which is just another version of the flux self-compensation), current and magnetic field penetrate inside the superconductor by only a small distance (called the *London*

¹³ One more bad, though common, term – a wire can (super)conduct, but a quantum hardly can!

penetration depth) $\delta_L \sim 10^{-7}$ m.¹⁴ If the loop is made of a superconducting wire that is considerably thicker than δ_L , we can draw a contour deep inside the wire, at that the current density is negligible. According to Eq. (28), everywhere at the contour,

$$\nabla\varphi - \frac{q}{\hbar}\mathbf{A} = 0. \quad (3.39)$$

Integrating this equation along the contour as before (from point 1 to the virtually coinciding point 2), we need to have the phase difference $\varphi_{12} = 2\pi n$, because the wavefunction $\psi \propto \exp\{i\varphi\}$ in the initial and final points 1 and 2 should be “essentially” the same, i.e. produce the same observables. As a result, we get

$$\Phi = \oint_C \mathbf{A} \cdot d\mathbf{r} = \frac{2\pi\hbar}{q} n = \frac{\pi\hbar}{e} n = n\Phi_0. \quad (3.40) \quad \text{Flux quantization}$$

This is the famous *flux quantization effect*,¹⁵ which justifies the term “magnetic flux quantum” for the constant Φ_0 given by Eq. (38).

Here I have to mention in passing very interesting effects of “partial flux quantization”, that arise when a superconductor loop is closed by a Josephson junction, forming the so-called *Superconductor QUantum Interference Device* - “SQUID”. Such devices are used, in particular, for supersensitive magnetometry and ultrafast, low-power computing.¹⁶

3.2. Landau levels and quantum Hall effect

In the last section, we have used the Schrödinger equation (27) for analysis of static magnetic field effects in “almost-1D”, circular geometries shown in Figs. 1, 2, and 4. However, this equation describes very interesting effects in higher dimensions as well, especially in the 2D case. Let us consider a uniform 2D quantum well (say, parallel to the $[x, y]$ plane), with strong confinement in the perpendicular direction z . According to the discussion in Sec. 1.6, energy-relaxed particles will always reside in the lowest energy subband, with constant quantization energy $(E_z)_1$. Adding this shift to well’s flat floor $U(x, y) = \text{const}$, and taking the resulting constant energy as the reference, for the 2D motion of the particle in the well, we reduce Eq. (27) to the similar equation, but with the Laplace operator acting only in directions x and y :

$$-\frac{\hbar^2}{2m} \left(\mathbf{n}_x \frac{\partial}{\partial x} + \mathbf{n}_y \frac{\partial}{\partial y} - i \frac{q}{\hbar} \mathbf{A} \right)^2 \psi = E \psi. \quad (3.41)$$

Let us find its solutions for the simplest case when the applied static magnetic field is uniform and perpendicular to the plane:

$$\mathcal{B} = \mathcal{B} \mathbf{n}_z. \quad (3.42)$$

¹⁴ For more detail, see EM Sec. 6.3.

¹⁵ It was predicted in 1949 by F. London and experimentally discovered (independently and virtually simultaneously) in 1961 by two experimental groups: B. Deaver and W. Fairbank, and R. Doll and M. Näbauer.

¹⁶ A brief review of these effects, and recommendations for further reading may be found in EM Sec. 6.4.

According to the second of Eqs. (21), this imposes the following restriction on the choice of vector-potential:

$$\mathcal{B} = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}, \quad (3.43)$$

but the gauge transformations still give us a lot of freedom in its choice. The “natural” axially-symmetric form, $\mathbf{A} = \mathbf{n}_\varphi \rho \mathcal{B}/2$, where $\rho = (x^2 + y^2)^{1/2}$ is the distance from some z -axis, leads to a cumbersome math. In 1930, L. Landau realized that the energy spectrum of Eq. (41) may be obtained by making a very simple choice

$$A_x = 0, \quad A_y = \mathcal{B}(x - x_0), \quad (3.44)$$

(with arbitrary x_0), which evidently satisfies Eq. (43), though it ignores the physical equivalence of the x and y directions. Now, expanding the eigenfunction into the Fourier integral in direction y :

$$\psi(x, y) = \int X_k(x) e^{ik(y - y_0)} dk, \quad (3.45)$$

we see that for each component of this integral, Eq. (41) yields a specific equation

$$-\frac{\hbar^2}{2m} \left[\mathbf{n}_x \frac{d}{dx} + i \mathbf{n}_y \left(k - \frac{q}{\hbar} \mathcal{B}(x - x_0) \right) \right]^2 X_k = E X_k. \quad (3.46)$$

Since the vectors inside the square brackets are mutually perpendicular, its square has no crossterms, so that Eq. (46) may be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} X_k + \frac{\hbar^2}{2m} \left[\frac{q}{\hbar} \mathcal{B}(x - x_0') \right]^2 X_k = E X_k, \quad \text{where } x_0' \equiv x_0 + \frac{\hbar k}{q \mathcal{B}}. \quad (3.47)$$

But this 1D Schrödinger equation is identical to Eq. (2.268) for the 1D harmonic oscillator, but with the center at point x_0' , and frequency ω_0 equal to

$$\omega_c = \frac{|q| \mathcal{B}}{m}. \quad (3.48)$$

In this expression, it is easy to recognize the classical *cyclotron frequency* of particle's motion in the magnetic field. (It may be readily obtained using the 2nd Newton law for a circular orbit of radius r ,

$$m \frac{v^2}{r} = F_{\mathcal{B}} = qv\mathcal{B}, \quad (3.49)$$

and noting that the resulting ratio $v/r = q\mathcal{B}/m$ is just the radius-independent angular velocity ω_c of particle's rotation.) Hence, the energy spectrum for each Fourier component of integral (45) is the same:

$$E_n = \hbar \omega_c \left(n + \frac{1}{2} \right), \quad (3.50)$$

and does not depend on either x_0 , or y_0 , or k .

This is an example of a highly *degenerate* system: for each eigenvalue E_n , there are many different eigenfunctions that differ by the positions $\{x_0, y_0\}$ of their center on axis x , and the rate k of

their phase change along axis y . They may be used to assemble a large variety of linear combinations, including 2D wave packets whose centers move along classical circular orbits with some radius r determined by initial conditions. Note, however, that such radius cannot be smaller than the so-called *Landau radius*,

$$r_L \equiv \left(\frac{\hbar}{q\mathcal{B}} \right)^{1/2}, \quad (3.51) \quad \text{Landau radius}$$

which characterizes the minimum radius of the wave packet itself, and results from Eq. (2.271) after replacement (48). This radius is remarkably independent on particle's mass, and may be interpreted in the following way: the scale $\mathcal{B}A_{\min}$ of the applied magnetic field's flux through the effective area $A_{\min} = 2\pi r_L^2$ of the smallest wave packet is just one normal flux quantum $\Phi_0' = 2\pi\hbar/q$.

A detailed analysis of such wave packets (for which we would not have time in this course) shows that magnetic field does not change the *average* density dN_2/dE of different 2D states on the energy scale, but just “assembles” them on the Landau levels (see Fig. 5a), so that the number of states on each Landau area (per unit area) is

$$n_L \equiv \frac{N_2}{A} = \frac{1}{A} \frac{dN_2}{dE} \Big|_{\mathcal{B} \neq 0} \Delta E = \frac{1}{A} \frac{dN_2}{dE} \Big|_{\mathcal{B}=0} \Delta E = \frac{m}{2\pi\hbar^2} \hbar\omega_c = \frac{q\mathcal{B}}{2\pi\hbar} = \frac{q\mathcal{B}}{h}. \quad (3.52)$$

This expression may again be interpreted in terms of magnetic flux quanta: $n_L\Phi_0' = \mathcal{B}$, i.e. there is one particular state on each Landau level per each flux quantum.

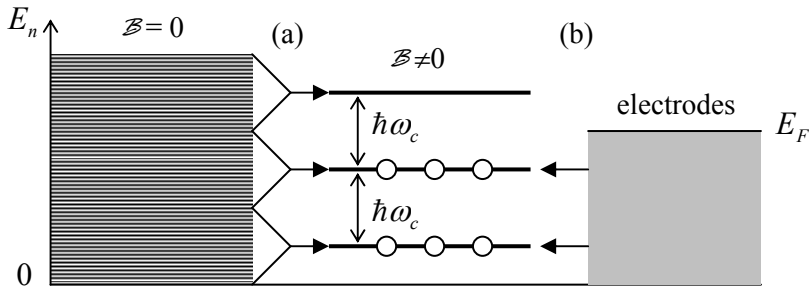


Fig. 3.5. (a) “Condensation” of 2D states on Landau levels, and (b) filling the levels by external electrons at the quantum Hall effect.

The most famous application of the Landau levels concept is the explanation of the *quantum Hall effect*¹⁷. Generally, the Hall effect¹⁸ is observed in the geometry sketched in Fig. 6, where electric current I is passed through a thin rectangular conducting sample (frequently called the *Hall bar*) placed into a magnetic field $\mathcal{B}$ perpendicular to the sample plane. The classical analysis of the effect is based on the notion of the Lorentz force (14). This force deviates charge carriers (say, electrons) from their straight motion from one external electrode to another, bending them to the isolated edges of the bar (in Fig. 6, parallel to axis x). Here the carriers accumulate, generating a gradually increasing electric field $\mathcal{E}$, until its force (16) exactly balances the Lorentz force (14):

¹⁷ It was first observed in 1980 by K. von Klitzing and coworkers.

¹⁸ Discovered in 1879 by E. Hall.

$$q\mathcal{E}_y = qv_x\mathcal{B}, \quad (3.53)$$

where v_x is the drift velocity of the electrons along the bar (Fig. 6), providing the sustained balance condition $\mathcal{E}_y/v_x = \mathcal{B}_z$ at each point of the 2D sample.

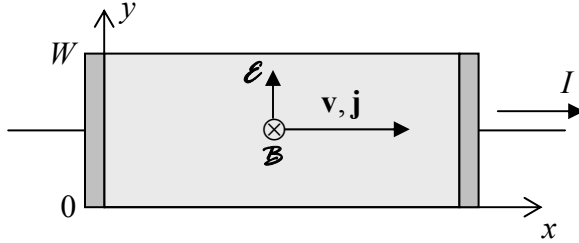


Fig. 3.6. Hall bar geometry. Darker rectangles show external (3D) electrodes.

With n_2 carriers per unit area, in a sample of width W , this condition yields the following classical expression for the so-called *Hall resistance* R_H :

$$R_H \equiv \frac{V_y}{I_x} = \frac{\mathcal{E}_y W}{qn_2 v_x W} = \frac{\mathcal{B}}{qn_2}. \quad (3.54)$$

Classical
Hall
effect

This formula is broadly used in practice for the measurement of the carrier density n_2 , and (in semiconductors) the carrier type – negative electrons or positive holes.

However, in experiments with high-quality (low-defect) 2D quantum wells at very low, sub-kelvin temperatures¹⁹ and high magnetic fields, the linear growth of R_H with $\mathcal{B}$, described by Eq. (54), is interrupted by virtually horizontal plateaus (Fig. 7) with constant values

$$R_H = \frac{1}{i} R_K, \quad (3.55)$$

where i (only in this context, following tradition!) is an integer, and value

$$R_K \approx 25.812807557 \text{ k}\Omega \quad (3.56)$$

is reproduced with extremely high accuracy ($\sim 10^{-9}$) from experiment to experiment and from sample to sample. Such stability is a very rare exception in solid state physics where most results are noticeably dependent on the particular material and particular sample under study.

Let us apply the Landau level picture. The 2D sample is typically in a weak contact with 3D electrodes whose conductivity electrons form a Fermi sea with certain Fermi energy E_F , so that at low temperatures all states with $E < E_F$ are filled with electrons – see Fig. 5b. As $\mathcal{B}$ is increased, spacing $\hbar\omega_c$ between the Landau levels increases, so that fewer and fewer of these levels are below E_F and are filled, and within broad ranges of field variation, the number i of filled levels is constant. (In Fig. 5b, $i = 2$.) So, plugging $n_2 = in_L$ and $q = \pm e$ into Eq. (54), we get

$$R_H = \frac{1}{i} \frac{\mathcal{B}}{qn_L} = \frac{1}{i} \frac{2\pi\hbar}{e^2} = \frac{1}{i} \frac{h}{e^2}, \quad (3.57)$$

Quantum
Hall
effect

¹⁹ Recently, the quantum Hall effect was observed at room temperature in the *graphene* (a virtually perfect 2D sheet of carbon atoms, see Sec. 4 below) – see K. Novoselov *et al.*, *Science* **315**, 1379 (2007).

i.e. exactly the experimental result (55), with

$$R_K = \frac{h}{e^2} \equiv 4 \frac{\pi \hbar}{2e^2}. \quad (3.58)$$

This constant, exactly 4 times the quantum unit of resistance R_Q given by Eq. (2.259), is in an excellent agreement with experimental value (56), and is sometimes called the *Klitzing constant*.

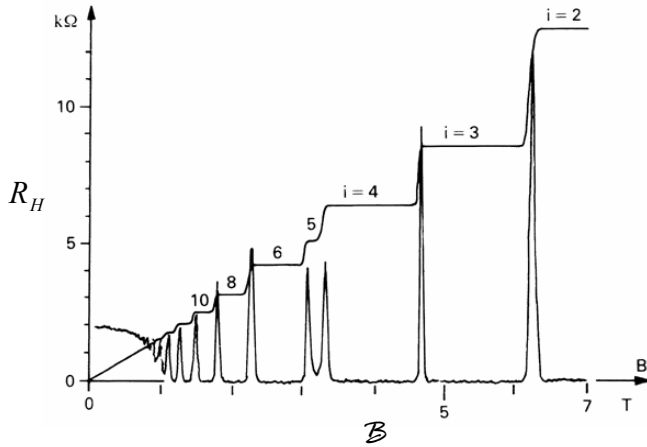


Fig. 3.7. Typical record of the quantum Hall effect. The lower trace (with sharp peaks) shows the longitudinal component, V_x/I_x , of the resistance tensor. (Adapted from www.prequark.org/Prequark.htm.)

However, this oversimplified explanation of the quantum Hall effect does not take into account several important factors, including:

(i) the role of nonuniformity of the quantum well bottom potential $U(x, y)$, and of the localized states this nonuniformity produces, and the surprisingly small effect of these factors on the extraordinary accuracy of Eq. (55);²⁰ and

(ii) the mutual Coulomb interaction of the electrons, in high-quality samples leading to the formation of R_H plateaus with not only integer, but also fractional values of i ($1/3$, $2/5$, $3/7$, etc.).²¹

Unfortunately, a thorough discussion of these interesting features is well beyond the framework of this course.²²

3.3. Scattering and diffraction

The second class of quantum effects that become more rich in multi-dimensional space is typically referred to as either *diffraction* or *scattering* - depending on the context. (Diffraction is essentially the interference, but of waves emitted by several many coherent sources.) Just as in the two –

²⁰ The explanation of this paradox may be obtained in terms of the so-called *quantum edge channels* – the quasi-1D regions of width (51), along the lines where the Landau levels cross the Fermi surface. Particle motion along these channels, which is responsible for electron transfer, is effectively one-dimensional and thus cannot be affected by modest uniformities of the potential distribution $U(x, y)$.

²¹ This *fractional quantum Hall effect* was discovered in 1982 by D. Tsui, H. Stormer, and A. Gossard. In contrast, the effect described by Eq. (55) with integer i (Fig. 7) is now called the *integer quantum Hall effect*.

²² For a comprehensive discussion of these effects I can recommend, e.g., either the monograph by D. Yoshioka, *The Quantum Hall Effect*, Springer, 1998, or the review by D. Yennie, *Rev. Mod. Phys.* **59**, 781 (1987).

slits in the Young-type experiment (Fig. 1), these sources are most frequently the elementary re-emitters of some initial wave from a single source. More generally, such re-emitting is called scattering; this term is also applied to particles – even if their quantum properties may be ignored.²³

Figure 8 shows the general scattering situation. Most commonly, the detector of scattered particles (in the quantum case, read de Broglie waves) is located at a large distance $r \gg a$ from the scatterer.²⁴ In this case, the main observable independent of r is the *flux* (number of particles per unit time) of particles scattered in a certain direction, i.e. their flux per unit solid angle. Since such flux is proportional to the incident flux of particles per unit area, the ability of the scatterer to re-emit in a particular direction may be characterized by the ratio of these two fluxes. This ratio has the dimensionality of area per unit angle, and is called the *differential cross-section* of the scatterer:

$$\frac{d\sigma}{d\Omega} \equiv \frac{\text{flux of scattered particles per unit solid angle}}{\text{flux of incident particles per unit area}}. \quad (3.58)$$

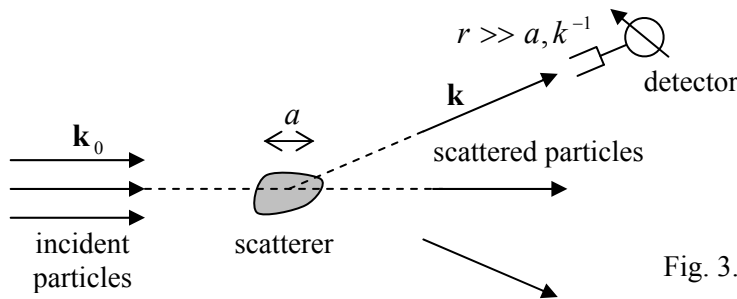


Fig. 3.8. 3D scattering (schematically).

Such name and notation stem from the fact that the integral of $d\sigma/d\Omega$ over all scattering angles,

$$\sigma \equiv \oint \frac{d\sigma}{d\Omega} d\Omega = \frac{\text{total flux of scattered particles}}{\text{incident flux per unit area}}, \quad (3.59)$$

(also with the dimensionality of area), has a simple interpretation as the *full cross-section* of scattering. For the simplest case when a macroscopic solid object scatters all classical particles hitting its surface, but does not affect the particles flying by it, σ is just the geometrical cross-section of the object, as visible from the direction of incoming particles.

In classical mechanics,²⁵ we first calculate the particle scattering angle as a function of the *impact parameter* b , and then average the result over all values of b , considered random. In this sense the calculations in wave mechanics are simpler, because a parallel beam of incident particles of fixed energy E may be fairly presented by a plane de Broglie wave

$$\psi_0 = a_0 e^{i\mathbf{k}_0 \cdot \mathbf{r}}, \quad (3.60)$$

²³ See, e.g., CM Sec. 3.7.

²⁴ In optics, this limit is called the *Fraunhofer diffraction* – see, e.g., EM Secs. (8.6) and (8.8).

²⁵ For example, in the simplest task of derivation of the so-called *Rutherford formula* for scattering of a charged nonrelativistic particle by a point fixed charge, due to their Coulomb interaction – see, e.g., CM Sec. 3.7.

with the free-space wave number $k_0 = (2mE)^{1/2}/\hbar$ and constant probability current density (1.49):

$$\mathbf{j}_0 = |a_0|^2 \frac{\hbar}{m} \mathbf{k}_0. \quad (3.61)$$

This current density is exactly the flux of incident particles per unit area that is used in the denominator of definition (58), so the “only” remaining thing to do is to calculate the nominator of that fraction.

To do this, let us write the Schrödinger equation for the scattering problem (now in the whole space including the scatterer) in the form

$$(E - \hat{H}_0)\psi = U(\mathbf{r})\psi, \quad (3.62)$$

where

$$\hat{H}_0 \equiv -\frac{\hbar^2}{2m} \nabla^2, \quad \text{and} \quad E = \frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m}. \quad (3.63)$$

the potential energy $U(\mathbf{r})$ describes the effect of scatterer. Looking for the solution of Eq. (62) in the natural form

$$\psi = \psi_0 + \psi_s, \quad (3.64)$$

where ψ_0 is the incident wave (60), and ψ_s has the sense of the scattered wave, and taking into account that former wave satisfies the free-space equation

$$\hat{H}_0 \psi_0 = E \psi_0, \quad (3.65)$$

we may reduce Eq. (62) to

$$(E - \hat{H}_0)\psi_s = U(\mathbf{r})(\psi_0 + \psi_s). \quad (3.66)$$

The most straightforward (and common) simplification of this problem is possible if the scattering potential $U(\mathbf{r})$ is in some sense weak. (We will derive the exact condition of this smallness below.) Then since at $U(\mathbf{r}) = 0$ the scattering wave ψ_s disappears, we may expect that at small but nonvanishing $U(\mathbf{r})$, the main part of ψ_s is proportional to its scale U_0 . Then all terms in Eq. (66) are proportional to U_0 , besides the product $U\psi_s$, which is proportional to U_0^2 . Hence, in the first approximation in U_0 , that term may be ignored, and Eq. (66) reduces to the famous equation of the *Born approximation*:²⁶

$$(E - \hat{H}_0)\psi_s = U(\mathbf{r})\psi_0. \quad (3.67a) \quad \text{Born approximation}$$

This simplification changes the situation drastically, because the linear superposition principle allows finding an explicit solution of this equation (in the form of an integral) for an *arbitrary* function $U(\mathbf{r})$. Indeed, after rewriting Eq. (67a) as

²⁶ Named after M. Born, who was the first one to apply this approximation in quantum mechanics. However, the basic idea of this approach had been developed much earlier (in 1881) by Lord Rayleigh in the context of electromagnetic wave scattering – see, e.g., EM Sec. 8.3. Note that the contents of that section repeats much of our current discussion – regrettably but unavoidably so, because the Born approximation is a centerpiece of scattering theory for both electromagnetic and de Broglie waves.

$$(\nabla^2 + k^2)\psi_s = \frac{2m}{\hbar^2}U(\mathbf{r})\psi_0(\mathbf{r}), \quad (3.67b)$$

we may notice that ψ_s is just a response of a linear system to a certain “excitation” (represented by the right-hand part) that is fixed, i.e. does not depend on the solution. Hence we can present ψ_s as a sum of responses to elementary excitations from elementary volumes d^3r' :

$$\psi_s(\mathbf{r}) = \frac{2m}{\hbar^2} \int U(\mathbf{r}')\psi_0(\mathbf{r}')G(\mathbf{r}, \mathbf{r}')d^3r'. \quad (3.68)$$

Spatial
Green's
function

Here $G(\mathbf{r}, \mathbf{r}')$ is the *spatial Green's function*, defined as such an elementary response of the free-space Schrödinger equation to a point excitation, i.e. the solution of the following equation²⁷

$$(\nabla^2 + k^2)G = \delta(\mathbf{r} - \mathbf{r}'). \quad (3.69)$$

But we already know the physically-relevant spherically-symmetric solution of this equation – see Eq. (7) and its discussion:

$$G(\mathbf{r}, \mathbf{r}') = \frac{f_+}{R} e^{ikR}, \quad (3.70)$$

so that we need just to calculate the coefficient f_+ for Eq. (67). This can be done in several ways, for example by noticing that at $r \ll k^{-1}$, the second term in Eq. (70) is negligible, and it is reduced to the well-known Poisson equation with delta-functional right-hand part, which describes, for example, the electrostatic potential generated by a point electric charge. Either recalling the Coulomb law, or applying the Gauss theorem,²⁸ we readily get the asymptote

$$G \rightarrow -\frac{1}{4\pi R}, \quad \text{at } kr \ll 1, \quad (3.71)$$

which is compatible with Eq. (70) only if $f_+ = -1/4\pi$, i.e. if

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi R} e^{ikR}. \quad (3.72)$$

Green's
function
for free
space

Plugging this result into Eq. (68), we get the final solution of Eq. (67):

$$\psi_s(\mathbf{r}) = -\frac{m}{2\pi\hbar^2} \int U(\mathbf{r}') \frac{\psi_0(\mathbf{r}')}{R} e^{ikR} d^3r'. \quad (3.73)$$

Note that if function $U(\mathbf{r})$ is smooth, the singularity in the denominator is integrable (i.e. not dangerous); indeed, the contribution of a sphere of radius $\mathcal{R} \rightarrow 0$, with the center in point $\mathbf{r}' = 0$, scales as

$$\int_{R < \mathcal{R}} \frac{d^3R}{R} = 4\pi \int_0^{\mathcal{R}} \frac{R^2 dR}{R} = 4\pi \int_0^{\mathcal{R}} R dR = 2\pi \mathcal{R}^2 \rightarrow 0. \quad (3.74)$$

²⁷ Please notice both the similarity and difference between this Green's function and the propagator discussed in Sec. 2.1. In both cases, we use the linear superposition principle to solve wave equations, but while Eq. (68) gives the solution of the *inhomogeneous* equation (67), Eq. (2.44) does that for a *homogeneous* Schrödinger equation in which the wave sources are presented by initial conditions rather than by equation's right-hand part.

²⁸ See, e.g., EM Sec. 1.2.

Actually, Eq. (73) gives us *more* than we wanted: it evaluates the scattered wave at *any* point, including those within of the scattering object, while our goal was to find the wave *far* from the scatterer – please revisit Fig. 8 if you need. However, before going to that limit, we can use the general formula to find the quantitative criterion of the Born approximation's validity. Indeed, let us estimate the magnitude of the right hand part of this equation, for a scatterer of linear size $\sim a$, and the potential magnitude scale U_0 , in two limits:

(i) If $ka \ll 1$, then inside the scatterer (i.e., at distances $r' \sim a$), both $\psi_0 \sim \exp\{ikr\}$ and the second exponent under the integral change slowly, so that a crude estimate of the solution is

$$|\psi_s| \sim \frac{m}{2\pi\hbar^2} U_0 |\psi_0| a^2. \quad (3.75)$$

(ii) In the opposite limit $ka \gg 1$, the integration along one of the dimensions (that of the wave propagation) is cut out on distances of the order of the de Broglie wavelength k^{-1} , so that the integral is correspondingly smaller:

$$|\psi_s| \sim \frac{m}{2\pi\hbar^2} U_0 |\psi_0| \frac{a^2}{ka}. \quad (3.76)$$

Since the reduction of Eq. (66) to Eq. (67) requires $|\psi_s| \ll |\psi_0|$ everywhere within the scatterer, we may now formulate the conditions of this requirement as

$$U_0 \ll \frac{\hbar^2}{ma^2} \max[ka, 1]. \quad (3.77)$$

In the first factor of the right-hand part, we may readily recognize the scale of the kinetic (quantum-confinement) energy E_a of the particle inside a quantum well of size $\sim a$, so that the Born approximation is valid essentially if the potential energy of particle's interaction with the scatterer is smaller than E_a . Note, however, that estimates (75) and (76) are not valid in special situations when the effects of scattering *accumulate* in some direction. This is frequently the case for small scattering angles in extended objects (when $ka \gg 1$ but $ka\theta < 1$), and especially in 1D (or quasi-1D) scatterers oriented along the incident particle beam.

Now let us proceed to large distances $r \gg r' \sim a$, and simplify Eq. (73) using an approximation similar to the dipole expansion in electrodynamics.²⁹ In denominator's R , we can merely ignore r' in comparison with r , but the exponent requires more care, because even if $r' \sim a \ll r$, the product $kr' \sim ka$ may still be larger than 1. In the first approximation in r' , we can take (Fig. 9a):

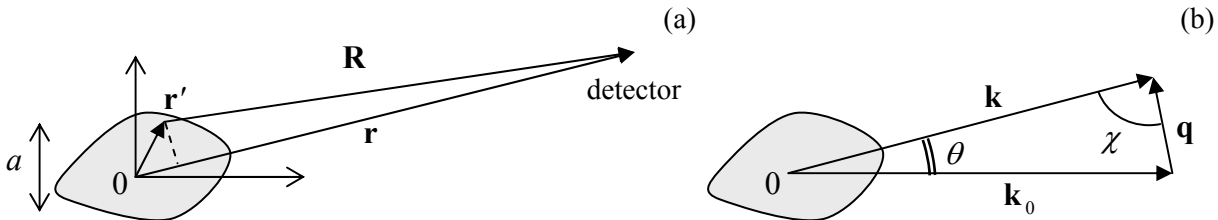


Fig. 3.9. (a) Dipole expansion in the Born approximation and (b) definitions of vector $\mathbf{q}$ and angles χ and θ .

²⁹ See, e.g., EM Sec. 8.2.

$$R \equiv |\mathbf{r} - \mathbf{r}'| \approx r - \mathbf{n}_r \cdot \mathbf{r}', \quad (3.78)$$

and since the directions of vectors $\mathbf{k}$ and $\mathbf{r}$ coincide, i.e. $\mathbf{k} = k\mathbf{n}_r$,

$$kR \approx kr - \mathbf{k} \cdot \mathbf{r}', \quad \text{and} \quad e^{ikR} \approx e^{ikr} e^{-i\mathbf{k} \cdot \mathbf{r}'}, \quad (3.79)$$

With this replacement, and the incident wave in form (60), the Born approximation yields

$$\psi_s(\mathbf{r}) = -\frac{m}{2\pi\hbar^2} \frac{a_0}{r} e^{ikr} \int U(\mathbf{r}') e^{-i(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}'} d^3r'. \quad (3.80)$$

This relation may be presented in a general form³⁰

Scattering
function

$$\psi_s = a_0 \frac{f(\mathbf{k}, \mathbf{k}_0)}{r} e^{ikr}, \quad (3.81)$$

where $f(\mathbf{k}, \mathbf{k}_0)$ is called the *scattering function*.³¹ Its physical sense becomes clear from the calculation of the corresponding probability current density $\mathbf{j}_s$. For that, generally we need to use Eq. (1.47) with the gradient operator having all spherical-coordinate components.³² However, at $kr \gg 1$ the main contribution to $\nabla \psi_s$, proportional to $k \gg 1/r$, is provided by the term $\exp\{ikr\}$ which changes fast in the common direction of vectors $\mathbf{r}$ and $\mathbf{k}$, so that

$$\nabla \psi_s \approx \mathbf{n}_r \frac{\partial}{\partial r} \psi_s \approx \mathbf{k} \psi_s, \quad \text{at } kr \gg 1. \quad (3.82)$$

so that Eq. (1.47) yields

$$\mathbf{j}_s(\theta) \approx \frac{\hbar}{m} |a_0|^2 \frac{|f(\mathbf{k}, \mathbf{k}_0)|^2}{r^2} \mathbf{k}. \quad (3.83)$$

Since this vector is parallel to $\mathbf{k}$ and hence to $\mathbf{r}$, the flux in the nominator of Eq. (58), i.e. the probability current per unit solid angle, is just $r^2 j_s$. Hence, the differential cross-section is simply

$$\frac{d\sigma}{d\Omega} = \frac{j_s r^2}{j_0} = |f(\mathbf{k}, \mathbf{k}_0)|^2, \quad (3.84)$$

and the total cross-section is

$$\sigma = \oint |f(\mathbf{k}, \mathbf{k}_0)|^2 d\Omega, \quad (3.85)$$

so that the scattering function $f(\mathbf{k}, \mathbf{k}_0)$ gives us everything we need (and in fact more, because the function also contains information about the phase of the scattered wave).

³⁰ It is easy to prove that this form is an asymptotic form of *any* solution ψ_s of the scattering problem (even that beyond the Born approximation) at sufficiently large distances $r \gg a, k^{-1}$.

³¹ Note that function f has the dimension of length, and does not account for the incident wave. This is why sometimes a dimensionless function, $S = 1 + 2ikf$, is used instead. This function S is called the *scattering matrix*, because it may be considered as a natural generalization of the 1D matrix S , defined by Eq. (2.133), to higher dimensionality.

³² See, e.g., MA Eq. (10.8).

According to Eq. (80), in the Born approximation the scattering function may be presented as the *Born integral*

$$f(\mathbf{k}, \mathbf{k}_0) = -\frac{m}{2\pi\hbar^2} \int U(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d^3r, \quad (3.86)$$

where for the notation simplicity I have replaced $\mathbf{r}'$ with $\mathbf{r}$, and also introduced the *scattering vector*

$$\mathbf{q} \equiv \mathbf{k} - \mathbf{k}_0, \quad (3.87)$$

with length $q = 2k \sin(\theta/2)$, where θ is the *scattering angle* between vectors $\mathbf{k}$ and $\mathbf{k}_0$ – see Fig. 9b. For the differential cross-section, Eq. (86) yields

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2} \right)^2 \left| \int U(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d^3r \right|^2, \quad (3.88)$$

Differential cross-section in the Born approximation

and the total cross-section may be now readily calculated from the first of Eqs. (59).³³

This is the main result of this section; it may be further simplified for spherically-symmetric scatterers, with

$$U(\mathbf{r}) = U(r). \quad (3.89)$$

Here, it is convenient to present the exponent in the Born integral as $\exp\{-iqr' \cos \chi\}$, where χ is the angle between vectors $\mathbf{k}$ (i.e. the direction $\mathbf{n}_r$ toward the detector) and $\mathbf{q}$ (rather than the incident wave vector $\mathbf{k}_0$!) – see Fig. 9b. Now, for fixed $\mathbf{q}$, we can take this vector's direction as the polar axis of a spherical coordinate system, and reduce Eq. (86) to a 1D integral:

$$\begin{aligned} f(\mathbf{k}, \mathbf{k}_0) &= -\frac{m}{2\pi\hbar^2} \int r^2 dr U(r) \int_0^{2\pi} d\phi \int_0^\pi \sin \chi d\chi \exp\{-iqr' \cos \chi\} \\ &= -\frac{m}{2\pi\hbar^2} \int r^2 dr U(r) 2\pi \frac{2 \sin qr}{qr} = -\frac{2m}{\hbar^2 q} \int U(r) \sin(qr) r dr. \end{aligned} \quad (3.90)$$

As a simple example, let us use the Born approximation to analyze scattering on the following spherically-symmetric potential:

$$U(\mathbf{r}) = U_0 \exp\left\{-\frac{r^2}{2a^2}\right\}. \quad (3.91)$$

In this particular case, it is better to avoid the temptation to exploit the spherical symmetry by using Eq. (90), and instead use the generic Eq. (88), because it falls apart into a product of three similar Cartesian factors:

$$f(\mathbf{k}, \mathbf{k}_0) = -\frac{mU_0}{2\pi\hbar^2} I_x I_y I_z, \quad (3.92)$$

with

³³ Note that according to Eq. (88), in the Born approximation the scattering intensity does not depend on the sign of potential U , and also that scattering in a certain direction is completely determined by a specific Fourier harmonic of function $U(\mathbf{r})$, namely by the harmonic with the wave vector equal to the scattering vector $\mathbf{q}$.

$$I_x = \int_{-\infty}^{+\infty} \exp\left\{-\left(\frac{x^2}{2a^2} + iq_x x\right)\right\} dx, \quad (3.93)$$

and similar integrals for I_y and I_z . From Chapter 2, we already know that Gaussian integrals like I_x may be readily worked out by complementing the exponent to the full square, in our current case giving

$$I_x = (2\pi)^{1/2} a \exp\left\{-\frac{q_x^2 a^2}{2}\right\}, \quad \text{etc.}, \quad (3.94)$$

so that, finally,

$$\frac{d\sigma}{d\Omega} = |f(\mathbf{k}, \mathbf{k}_0)|^2 = \left(\frac{mU_0}{2\pi\hbar^2} I_x I_y I_z\right)^2 = 2\pi a^2 \left(\frac{mU_0 a^2}{\hbar^2}\right)^2 e^{-q^2 a^2}. \quad (3.95)$$

Now, the total cross-section σ is an integral of $d\sigma/d\Omega$ over all directions of vector $\mathbf{k}$. Since in our case the scattering intensity does not depend on the azimuthal angle φ , the integration is reduced to that over the scattering angle θ (Fig. 9b):

$$\begin{aligned} \sigma &\equiv \oint \frac{d\sigma}{d\Omega} d\Omega = 2\pi \int_0^\pi \frac{d\sigma}{d\Omega} \sin\theta d\theta = 4\pi^2 a^2 \left(\frac{mU_0 a^2}{\hbar^2}\right)^2 \int_0^\pi \sin\theta d\theta \exp\left\{-\left(2k \sin\frac{\theta}{2}\right)^2 a^2\right\} \\ &= 4\pi^2 a^2 \left(\frac{mU_0 a^2}{\hbar^2}\right)^2 \int_{\theta=0}^{\theta=\pi} \exp\{-2k^2 a^2 (1 - \cos\theta)\} d(1 - \cos\theta) = \frac{2\pi^2}{k^2} \left(\frac{mU_0 a^2}{\hbar^2}\right)^2 \left[1 - e^{-4k^2 a^2}\right]. \end{aligned} \quad (3.96)$$

Let us analyze these formulas. In the low-energy limit, $ka \ll 1$ (and hence $qa \ll 1$ for any scattering angle), the scattered wave is virtually isotropic: $d\sigma/d\Omega \approx \text{const}$ – a very typical feature of scattering by small objects, in any approximation. Notice that in this limit, the Born expression for σ ,

$$\sigma \approx 8\pi^2 a^2 \left(\frac{mU_0 a^2}{\hbar^2}\right)^2, \quad (3.97)$$

is only valid if σ is much smaller than the scale a^2 of the physical cross-section of the scatterer.

In the opposite, high-energy limit $ka \gg 1$, the scattering is dominated by small angles $\theta \approx q/k \sim 1/ka \sim \lambda/a$:

$$\frac{d\sigma}{d\Omega} \approx 2\pi a^2 \left(\frac{mU_0 a^2}{\hbar^2}\right)^2 \exp\left\{-k^2 a^2 \frac{\theta^2}{2}\right\}. \quad (3.98)$$

This is, again, very typical for diffraction. Notice, however, that due to the smooth character of the Gaussian potential (91), the diffraction pattern exhibits no oscillations; such oscillations of $d\sigma/d\Omega$ as function of angle naturally appear for potentials with sharp borders – see, e.g., Problems 2 and 3.

The Born approximation, while being very simple and used more often than any other scattering theory, is not without substantial shortcomings, as is clear from the following example. It is not too difficult to prove the following general *optical theorem*, valid for an arbitrary scatterer:

$$\text{Im } f(\mathbf{k}_0, \mathbf{k}_0) = \frac{k}{4\pi} \sigma. \quad (3.99)$$

Optical theorem

However, Eq. (86) shows that in the Born approximation, function f is purely real at $q = 0$ (i.e. $\mathbf{k} = \mathbf{k}_0$), and hence cannot satisfy the optical theorem. Even more evidently, it cannot describe such a simple effect as a dark shadow ($\psi \approx 0$) cast by an opaque object (say, with $U_0 \gg E$).

There are several ways to improve the Born approximation, while still holding the general idea of approximate treatment of U .

(i) Instead of the main assumption $\psi_s \propto U_0$, we can use a complete perturbation series:

$$\psi_s = \psi_1 + \psi_2 + \dots \quad (3.100)$$

with $\psi_n \propto U_0^n$, and find successive approximations ψ_n one by one. In the 1st approximation we of course return to the Born formula, but already the 2nd approximation yields

$$\text{Im } f_2(\mathbf{k}_0, \mathbf{k}_0) = \frac{k}{4\pi} \sigma_1, \quad (3.101)$$

where σ_1 is the full cross-section calculated in the 1st approximation, so that the optical theorem (99) is “almost” satisfied.³⁴

(ii) As was mentioned above, the Born approximation does not work very well for small-angle scattering by extended objects. This deficiency may be corrected by the so-called *eikonal approximation* (from Greek word εικον, meaning “icon”) that replaces the plane wave exponent $\exp\{ik_0 x\}$ representation of the incident wave by a WKB-like exponent, though still in the first nonvanishing approximation in $U \rightarrow 0$:

$$e^{ikx} \rightarrow \exp\left\{i \int_0^x k(x') dx'\right\} = \exp\left\{i \int_0^x \frac{\{2m[E - U(x')]\}^{1/2}}{\hbar} dx'\right\} \approx e^{ikx} - \frac{m}{\hbar^2 k} \int_0^x U(x') dx'. \quad (3.102)$$

Eikonal approximation

This approximation’s results satisfy the optical theorem (99) already in the 1st approximation in U .

3.4. Energy bands in higher dimensions

In Sec. 2.5, we have discussed the 1D band theory for potential profiles $U(x)$ that obey the periodicity condition (2.192). For what follows, let us notice that that condition may be rewritten as

$$U(x + X) = U(x), \quad (3.103)$$

³⁴ The construction of such series may be facilitated by the following observation. If we retain ψ_s in the right-hand part of Eq. (66), we may write a relation formally similar to Eq. (68) for the full wavefunction $\psi = \psi_0 + \psi_s$:

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \frac{2m}{\hbar^2} \int U(\mathbf{r}') \psi(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') d^3 r'.$$

This is one of forms of the *Lipmann-Schwinger equation* that is exactly equivalent to the differential Schrödinger equation (66) but is more convenient for some applications, in particular for the calculation of higher approximations ψ_n . Unfortunately, I will have not time to discuss this approach in detail and have to refer the reader, for example, to either Chapter 9 of the textbook by L. Schiff, *Quantum Mechanics*, 3rd ed., McGraw-Hill, 1968, or (for even more details) to monograph by J. Taylor, *Scattering Theory*, Dover, 2006.

where $X = \tau a$, with τ being an arbitrary integer. One can say that the set of points X forms a periodic *1D lattice* in the direct (x -) space. We have also seen that each Bloch state (i.e., each eigenstate of the Schrödinger equation for such periodic potential) is characterized by the quasi-momentum $\hbar q$ and its energy does not change if q is changed by a multiple of $2\pi/a$. Hence if we form, in the reciprocal (k -) space, a 1D lattice of points $Q = lb$, with $b = 2\pi/a$ and integer l , any pair of points from these two mutually reciprocal lattices satisfies the following rule:

$$\exp\{iQX\} = \exp\left\{il \frac{2\pi}{a} \tau a\right\} = e^{2\pi i \tau l} = 1. \quad (3.104)$$

In this form, the results of Sec. 2.5 may be readily extended to d -dimensional periodic potentials whose translational symmetry obeys the following generalization of Eq. (103):

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}), \quad (3.105)$$

where points $\mathbf{R}$, which may be numbered by d integers τ_j , form the so-called *Bravais lattice*³⁵ of points

$$\mathbf{R} = \sum_{j=1}^d \tau_j \mathbf{a}_j, \quad (3.106)$$

with d *primitive vectors* $\mathbf{a}_j$. The simplest example of a 3D Bravais lattice are given by the *simple cubic lattice* (Fig. 10a), which may be described by the system of mutually perpendicular primitive vectors $\mathbf{a}_j$ of equal length. However, not in any lattice these vectors are perpendicular; for example Figs. 10b and 10c show possible sets of the primitive vectors describing the *face-centered cubic lattice* (fcc) and *body-centered cubic lattice* (bcc). In 3D, the science of crystallography, based on the group theory, distinguishes, by their symmetry properties, 14 Bravais lattices grouped into 7 different *lattice systems*.³⁶

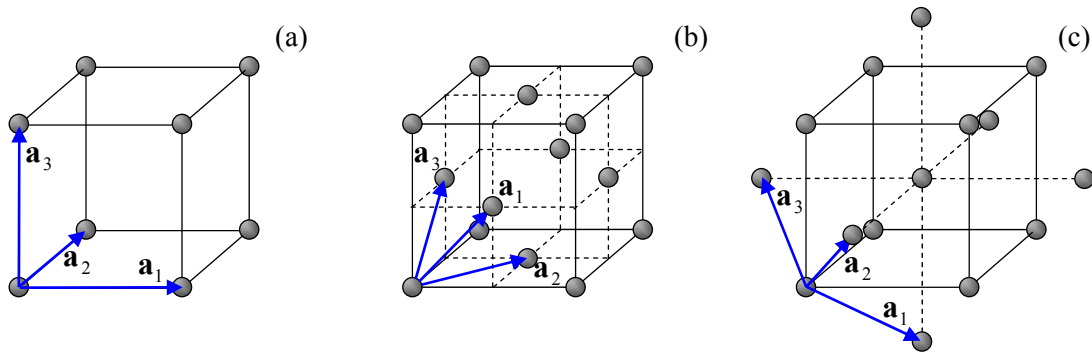


Fig. 3.10. The simplest (and most common) 3D Bravais lattices: (a) simple cubic, (b) face-centered cubic (fcc), and (c) body-centered cubic (bcc), and possible choices of their primitive vector sets (blue arrows).

Note, however, not all highly symmetric sets of points form Bravais lattices. As probably the most striking example, nodes of the very simple 2D *honeycomb lattice* (Fig. 11a) cannot be described by

³⁵ Named after A. Bravais, the crystallographer who introduced this notion in 1850.

³⁶ The strongest motivation for the band theory is provided by properties of solid crystals. Thus it is not surprising that perhaps the most clear, well illustrated introduction to the Bravais lattices may be found in Chapters 4 and 7 of the famous textbook by N. Ashcroft and N. Mermin, *Solid State Physics*, Saunders College, 1976.

a Bravais lattice - while the 2D hexagonal lattice, shown in Fig. 11b, can. The most prominent 3D case of such a lattice is the diamond structure (Fig. 11c), which describes, in particular, atoms of world's most important crystal – silicon.³⁷ In cases like these, the band theory is much facilitated by the fact that the Bravais lattices using some point assemblies (called *primitive unit cells*) may describe these point systems. For example, Fig. 11a shows the possible choice of primitive vectors for the honeycomb structure,³⁸ with the primitive unit cell formed by any two adjacent points of the original lattice (say, within the dashed ellipses in Fig. 11a). Similarly, the diamond lattice may be described as the fcc Bravais lattice with two-point primitive unit cell.³⁹

Now we are ready for the following generalization of the 1D Bloch theorem, given by Eqs. (2.193) and (2.210), to higher dimensions. Any eigenfunction of the Schrödinger equation describing particle's motion in the periodic potential (105) may be presented either as

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r})e^{i\mathbf{q} \cdot \mathbf{R}}, \quad (3.107)$$

or as

$$\psi(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{q} \cdot \mathbf{r}}, \quad \text{with } u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r}), \quad (3.108)$$

Two forms
of the 3D
Bloch
theorem

where the quasi-momentum $\hbar\mathbf{q}$ is again a constant of motion, but now is a vector.

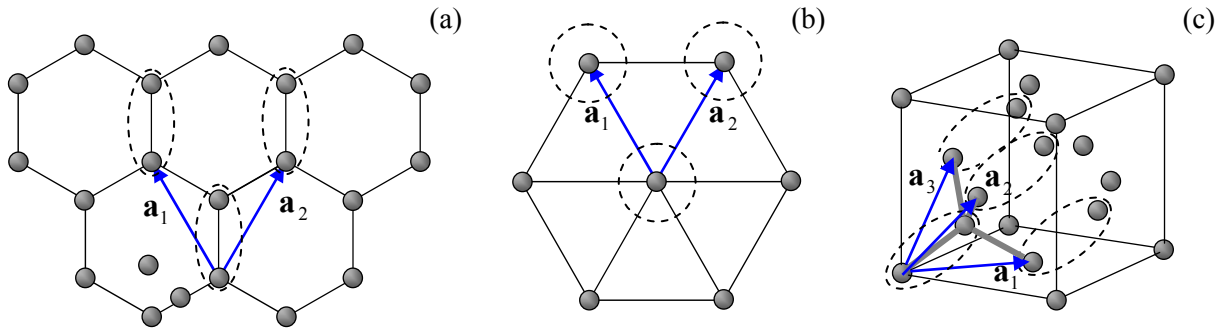


Fig. 3.11. Some important periodic structures that require two-point primitive cells for their Bravais lattice presentation: (a) 2D honeycomb lattice and their primitive vectors and (c) 3D diamond lattice. For a contrast, panel (b) shows the 2D hexagonal structure which forms a Bravais lattice with a single-point primitive cell.

The key notion of the band theory is the *reciprocal lattice* in the wavevector space, formed as

$$\mathbf{Q} = \sum_{j=1}^d l_j \mathbf{b}_j, \quad (3.109)$$

Reciprocal
lattice in
q-space

³⁷ It may be best understood as the sum of two fcc lattices of side a , mutually shifted by vector $\{1, 1, 1\}a/4$, so that the distances between each point of the combined lattice and its 4 nearest neighbors (see the thick gray lines in Fig. 11c) are all equal.

³⁸ This structure is presently very popular due to the recent discovery of *graphene* – isolated monolayer sheets of carbon atoms arranged in a honeycomb lattice with the interatomic distance of 0.142 nm.

³⁹ A harder case is presented by *quasicrystals* (whose idea may be traced down to medieval Islamic tilings, but was discovered in natural crystals, by D. Shechtman *et al.*, only in 1984), which obey high (say, 5-fold) rotational symmetry, but cannot be described by a Bravais lattice with any finite primitive unit cell. For a popular review of quasicrystals see, for example, P. Stephens and A. Goldman, *Sci. Amer.* **264**, #4, 24 (1991).

with integer l_j , and vectors $\mathbf{b}_j$ selected in such way that the following generalization of Eq. (104) is valid for any pair of points of the direct and reciprocal lattices:

$$e^{i\mathbf{Q}\cdot\mathbf{R}} = 1. \quad (3.110)$$

The importance of lattice $\mathbf{Q}$ is immediately clear from the first formulation of the Bloch theorem, given by Eq. (107): if we add to $\mathbf{q}$ any vector $\mathbf{Q}$ of the reciprocal lattice, the wavefunction does not change. This means that all information about the system is contained in just one elementary cell of the reciprocal space $\mathbf{q}$. Its most frequent choice, called the *1st Brillouin zone*, is the set of all points $\mathbf{q}$ that are closer to the origin than to any other point of lattice $\mathbf{Q}$.

It is easy to see that primitive vectors $\mathbf{b}_j$ of the reciprocal 3D lattice⁴⁰ may be constructed from those of the initial, direct lattice as

Primitive
vectors
of the
reciprocal
lattice

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}. \quad (3.111)$$

Indeed, from the “operand rotation rule” of the vector algebra⁴¹ it is evident that $\mathbf{a}_j \cdot \mathbf{b}_j = 2\pi \delta_{jj}$. Hence, the exponent in the left-hand part of Eq. (110) is reduced to

$$e^{i\mathbf{Q}\cdot\mathbf{R}} = \exp\{2\pi(l_1\tau_1 + l_2\tau_2 + l_3\tau_3)\}. \quad (3.112)$$

Since all l_j and τ_j are integers, the expression in the parentheses is also an integer, so the exponent indeed equals 1, thus satisfying the definition of the reciprocal lattice given by Eq. (110).

As the simplest example, let us return to the simple cubic lattice of period a (Fig. 10a), oriented in space so that

$$\mathbf{a}_1 = a\mathbf{n}_x, \quad \mathbf{a}_2 = a\mathbf{n}_y, \quad \mathbf{a}_3 = a\mathbf{n}_z, \quad (3.113)$$

According to Eq. (111), its reciprocal lattice is (of course) also cubic:

$$\mathbf{Q} = \frac{2\pi}{a}(l_x\mathbf{n}_x + l_y\mathbf{n}_y + l_z\mathbf{n}_z), \quad (3.114)$$

so that the 1st Brillouin zone is a cube with side $b = 2\pi/a$. Almost similarly simple calculations show that the reciprocal lattice of fcc is bcc, and vice versa. Figure 12 shows the resulting 1st Brillouin zone of the fcc lattice.

The notion of the reciprocal lattice⁴² makes the multi-dimensional band theory not much more complex than that in 1D, especially for numerical calculations, at least for the single-point Bravais lattices. Indeed, repeating all the steps that have led to Eq. (2.218), but now with a d -dimensional Fourier expansion of functions $U(\mathbf{r})$ and $u_l(\mathbf{r})$, we readily get its generalization:

$$\sum_{l' \neq l} U_{l'-l} u_{l'} = (E - E_l) u_l, \quad (3.115)$$

⁴⁰ For the 2D case ($j = 1, 2$), one may use, for example, the first two formulas of Eq. (111) with $\mathbf{a}_3 = \mathbf{a}_1 \times \mathbf{a}_2$.

⁴¹ See, e.g., MA Eq. (7.6).

⁴² This notion is also the main starting point of X-ray diffraction studies of crystals, because it allows rewriting the well-known Bragg condition for diffraction peaks in an extremely simple form of the momentum conservation law: $\mathbf{k} = \mathbf{k}_0 + \mathbf{Q}$, where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the, respectively, incident and diffracted photon.

where $\mathbf{l}$ is now a d -dimensional vector of integer indices l_j . The summation in Eq. (115) should be carried over all (essential) components of this vector (i.e. over all relevant nodes of the reciprocal lattice), so writing a corresponding computer code requires a bit more care than in 1D; however, this is just a homogeneous system of linear equations, and numerous routines of finding its eigenvalues E are readily available from both public sources and commercial software packages.⁴³

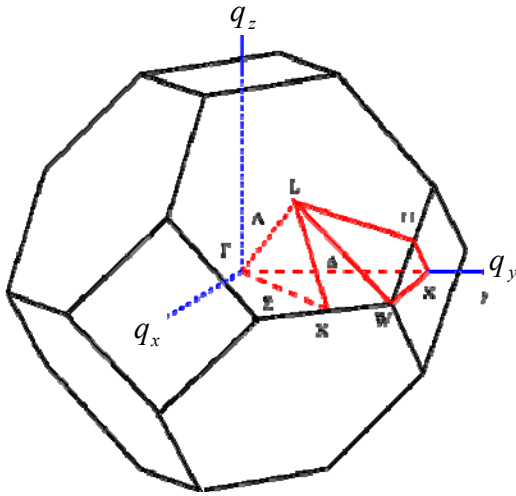


Fig. 3.12. 1st Brillouin zone of the fcc lattice, and the traditional notation of its main directions. Adapted from http://en.wikipedia.org/wiki/Band_structure.

What is indeed more complex than in 1D is the presentation (and hence the comprehension :-), of the calculation results and experimental data. Typically, the presentation is limited to plotting the Bloch state eigenenergy as a function of components of vector q along certain special directions the reciprocal space of quasi-momentum (see, e.g., the lines shown in Fig. 12), typically plotted on single panel. Figure 12 shows perhaps the most famous (and certainly the most practically important) of such plots, the band structure of silicon. The dashed horizontal lines mark the “indirect” gap of width 1.12 eV between the “valence” and “conduction” energy bands, which is the playground of virtually all silicon-based electronics.

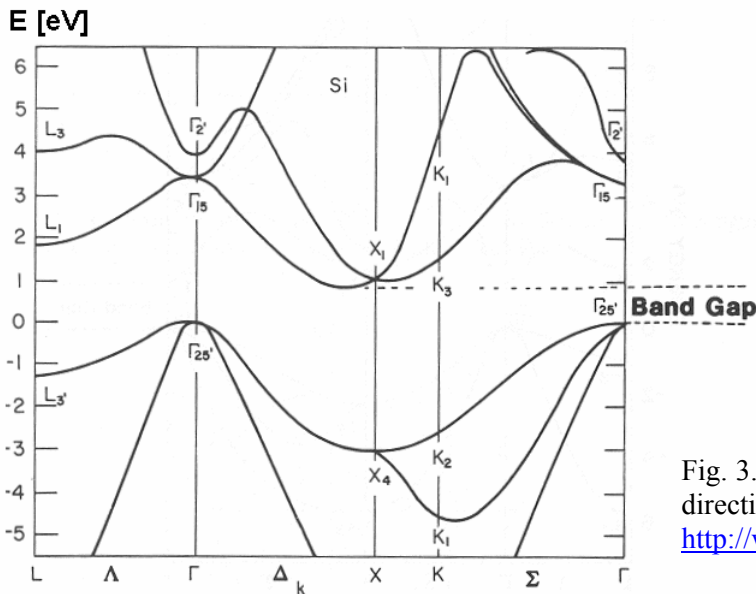


Fig. 3.13. Band structure of silicon, along the special directions shown in Fig. 12. (Adapted from http://www.tf.uni-kiel.de/matwis/amat/semi_en/.)

⁴³ See, e.g., MA Sec. 16 (iv).

In order to understand the reason of this band structure presentation complexity, let us see how we would start to develop the weak-potential approximation for the simplest case of a 2D square lattice (which is a subset of the cubic lattice, with $\tau_3 = 0$). Its 1st Brillouin zone is of course also a square, of area $(2\pi/a)^2$. Let us draw the lines of constant energy of a free particle ($U = 0$) in this zone. Repeating the arguments of Sec. 2.7 (see especially Fig. 2.28 and its discussion), we should conclude that Eq. (2.216) should now be generalized as follows,

$$E = E_1 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left[\left(q_x - \frac{2\pi l_x}{a} \right)^2 + \left(q_y - \frac{2\pi l_y}{a} \right)^2 \right], \quad (3.116)$$

with all possible integers l_x and l_y . Considering the result only within the 1st Brillouin zone, we see that as energy E grows, the lines of equal energy evolve as shown in Fig. 14. Just like in 1D, the weak-potential effects are only important at the Brillouin zone boundaries, and may be crudely considered as the appearance of narrow energy gaps, but one can see that the band structure in $\mathbf{q}$ -space is complex enough even without these effects.

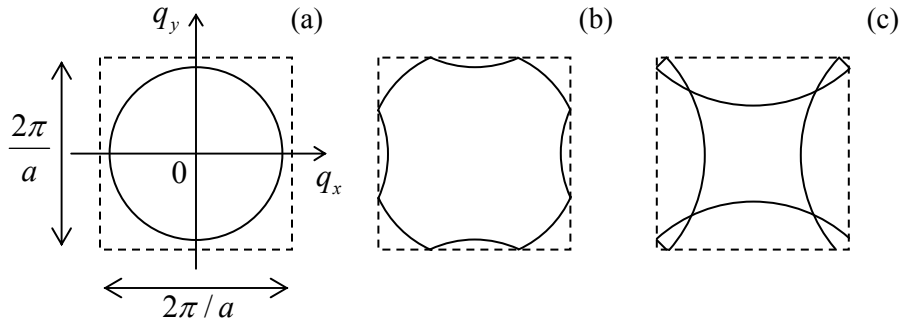


Fig. 3.14. Lines of constant energy E of a free particle, within the 1st Brillouin zone of a square Bravais lattice, for: (a) $E/E_1 \approx 0.95$, (b) $E/E_1 \approx 1.05$, and (c) $E/E_1 \approx 2.05$, where $E_1 \equiv \pi^2 \hbar^2 / 2ma^2$.

The tight-binding approximation is usually easier to follow. For example, for the same square 2D lattice, we may repeat the arguments that have led us to Eq. (2.203), to write ⁴⁴

$$i\hbar \frac{da_{0,0}}{dt} = -\delta_n (a_{-1,0} + a_{+1,0} + a_{0,+1} + a_{0,-1}), \quad (3.117)$$

where indices correspond to the deviations of integers τ_x and τ_y from an arbitrarily selected minimum of the potential energy - and hence wavefunction's "hump" quasi-localized at this minimum. Now, looking for the stationary solution of these equations, that corresponds to the Bloch theorem (107), instead of Eq. (2.206) we get

$$E = E_n + \varepsilon_n = E_n - \delta_n \left(e^{iq_x a} + e^{-iq_x a} + e^{iq_y a} + e^{-iq_y a} \right) = E_n - 2\delta_n (\cos q_x a + \cos q_y a). \quad (3.118)$$

Figure 15 shows this result, within the 1st Brillouin zone, in two forms: as the color-coded lines of equal energy and as a 3D plot (also enhanced by color).

⁴⁴ Actually, using the same values of δ_n in both directions implies some sort of symmetry of the quasi-localized states. For example, s -states of axially-symmetric potentials (see the next section) always have such a symmetry.

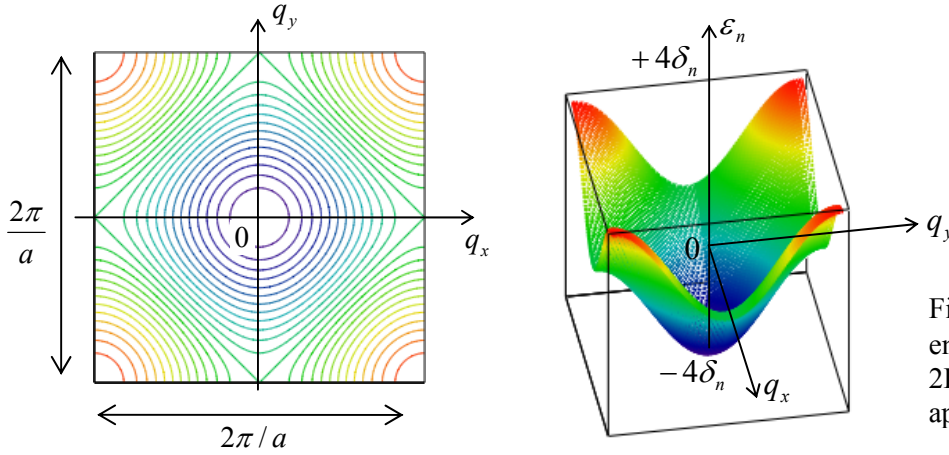


Fig. 3.15. Allowed band energy $\varepsilon_n = E - E_n$ for a square 2D lattice, in the tight-binding approximation.

It is evident that the plots of this function along different lines on the $\mathbf{q}$ -plane, for example along one of axes (say, q_x) and along a diagonal of the 1st Brillouin zone (say, $q_x = q_y$) give different curves, qualitatively similar to those of silicon (Fig. 13). The latter structure is complicated by the fact that the primitive cell of their Bravais lattices contains more than 2 atoms – see Fig. 11c and its discussion. In this case, even the tight-binding picture becomes more complex. Indeed, even if the atoms in the different positions of the primitive unit cell are similar (as they are, for example, in both graphene and silicon), and hence the potential well shape near those points and the corresponding local wavefunctions $u(\mathbf{r})$ are similar as well, the Bloch theorem (which only pertains to Bravais lattices!) does not forbid them to have different complex amplitudes $a(t)$ whose time evolution should be described by a specific differential equation.

For example, in order to describe the honeycomb lattice shown in Fig. 11a, we have to prescribe different amplitudes to the “top” and “bottom” points of its primitive cell – say, α and β , correspondingly. Since each of these points is surrounded (and hence weakly interacts) with 3 neighbors of the opposite type, instead of Eq. (117) we have to write two equations

$$i\hbar \frac{d\alpha}{dt} = -\delta_n \sum_{j=1}^3 \beta_j, \quad i\hbar \frac{d\beta}{dt} = -\delta_n \sum_{j'=1}^3 \alpha_{j'}, \quad (3.119)$$

where each summation is over 3 next-neighbor points. (I am using different summation indices just to emphasize that these directions are different for the “top” and “bottom” points of the primitive cell – see Fig. 11a.) Now using the Bloch theorem (107) in the form similar to Eq. (2.205), we get two coupled systems of linear algebraic equations:

$$(E - E_n)\alpha = -\delta_n \beta \sum_{j=1}^3 e^{i\mathbf{q}\cdot\mathbf{r}_j}, \quad (E - E_n)\beta = -\delta_n \alpha \sum_{j'=1}^3 e^{i\mathbf{q}\cdot\mathbf{r}'_{j'}}, \quad (3.120)$$

where $\mathbf{r}_j$ and $\mathbf{r}'_{j'}$ are the next-neighbor positions, as seen from the top and bottom points, respectively. Writing the condition of consistency of this system, we get two equal and opposite values for energy correction for each value of $\mathbf{q}$:

$$E_{\pm} = E_n \pm \delta_n \Sigma^{1/2}, \quad \text{where } \Sigma \equiv \sum_{j,j'=1}^3 e^{i\mathbf{q}\cdot(\mathbf{r}_j + \mathbf{r}'_{j'})}. \quad (3.121)$$

According to Eq. (120), these two energy bands correspond to the phase shifts (on the top of the regular Bloch shift $\mathbf{q} \cdot \Delta \mathbf{r}$) of either 0 or π between the adjacent quasi-localized wavefunctions $u(\mathbf{r})$.

The most interesting corollary of such energy symmetry, augmented by the honeycomb lattice symmetry, is that for certain values $\mathbf{q}_D$ of vector $\mathbf{q}$ (that turn out to be in each of 6 corners of the honeycomb-shaped 1st Brillouin zone), the double sum Σ vanishes, i.e. the two band surfaces $E_{\pm}(\mathbf{q})$ touch each other. As a result, in vicinities of these *Dirac points*⁴⁵ the dispersion relation is linear:

$$E_{\pm} \Big|_{\mathbf{q} \approx \mathbf{q}_D} \approx E_n \pm \hbar v_n |\tilde{\mathbf{q}}|, \quad \text{where } \tilde{\mathbf{q}} \equiv \mathbf{q} - \mathbf{q}_D, \quad (3.122)$$

with $v_n \propto \delta_n$ being a constant with the dimension of velocity (for graphene, close to 10^6 m/s). Such a linear dispersion relation ensures several interesting transport properties of graphene. For their discussion, I have to refer the reader to special literature.⁴⁶

3.5. Axially-symmetric systems

I cannot conclude this chapter (and hence our review of wave mechanics) without addressing the issue of eigenstates and eigenvalues at full confinement in multi-dimensional potentials $U(\mathbf{r})$. For an arbitrary potential, the stationary Schrödinger equation does not have an analytical solution, but a substantial symmetry of function $U(\mathbf{r})$ may make such solution possible. This pertains, in particular, to the axial symmetry in 2D problems and the spherical symmetry in 3D problems, which are typical for several important situations (or their reasonable models), especially in atomic and nuclear physics.

In rare cases such symmetry may be exploited by the separation of variables in Cartesian coordinates. The most famous example is the d -dimensional harmonic oscillator, i.e. a particle moving inside the potential

$$U = \frac{m\omega_0^2}{2} \sum_{j=1}^d r_j^2. \quad (3.123)$$

Separating the variables exactly as we did for the rectangular quantum well (see Sec. 1.5), for each degree of freedom we get the Schrödinger equation (2.268) of a 1D oscillator, whose eigenfunctions are given by Eq. (2.278), and the energy spectrum is described by Eq. (2.114). As a result, the total energy spectrum may be indexed by a vector $\mathbf{n} = \{n_1, n_2, \dots, n_d\}$ of d independent integers (quantum numbers):

$$E_{\mathbf{n}} = \hbar\omega_0 \left(\sum_{j=1}^d n_j + \frac{d}{2} \right), \quad (3.124)$$

⁴⁵ This term is based on a (pretty loose) analogy with the Dirac theory of relativistic quantum mechanics, to be discussed in Chapter 9 below. Namely, in the vicinity of a Dirac point (122), Schrödinger equations (119), and hence the dispersion relation (122), may be obtained from the effective Hamiltonian $\hat{H}_n = \hbar v_n \hat{\boldsymbol{\sigma}} \cdot \hat{\tilde{\mathbf{q}}}$. (Since vector $\tilde{\mathbf{q}}$ is two-dimensional, this Hamiltonian employs only two of three Pauli matrices.) This expression reminds the first term of Dirac's Hamiltonian (9.97), which is defined, however, in a different Hilbert space.

⁴⁶ See, e.g., a recent review by A. Castro Neto *et al.*, *Rev. Mod. Phys.* **81**, 109 (2009). Note that transport properties of graphene are determined by coupling of $2p_z$ electron states of carbon atoms, whose wavefunctions are proportional to $\exp\{\pm i\varphi\}$ rather than are axially-symmetric as implied by Eqs. (120). However, due to the lattice symmetry this fact does not affect the dispersion relation $E(\mathbf{q})$.

all of them ranging from 0 to ∞ . Note that every energy level of this system, with the only exception of the ground state,

$$\psi_g = \prod_{j=1}^d \psi_0(r_j) = \frac{1}{\pi^{d/4} x_0^{d/2}} \exp\left\{-\frac{1}{2x_0^2} \sum_{j=1}^d r_j^2\right\}, \quad (3.125)$$

is *degenerate*: several different wavefunctions, each with its own different set of quantum numbers n_j , but the same value of their sum, have the same energy.

However, the harmonic oscillator problem is an exception: for other central- and spherically-symmetric problems the solution is made easier by using more appropriate coordinates. Let us start with the simplest axially-symmetric problem: the so-called *planar rigid rotator* (or “rotor”), i.e. a particle constrained (confined) to move along a plane, round circle of radius R (Fig. 15).⁴⁷

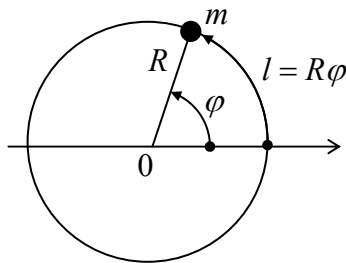


Fig. 3.16. Planar rigid rotator.

The planar rotator has just *one* degree of freedom, say the displacement arc $l = R\phi$. So, its classical energy (and Hamiltonian function) is $H = p_l^2/2m$, $p_l \equiv mv = m(dl/dt)$. This function is similar to that of a free 1D particle (with the replacement $x \rightarrow l$), and hence rotator's quantum properties may be described by a similar Hamiltonian operator:

$$\hat{H} = \frac{\hat{p}^2}{2m}, \quad \text{with} \quad \hat{p} = -i\hbar \frac{\partial}{\partial l}, \quad (3.126)$$

and its eigenfunctions have a similar structure:

$$\psi = Ce^{ikl}. \quad (3.127)$$

The “only” new feature is that in the rotator, all observables should be $2\pi R$ -periodic functions of l , and hence, as we have already discussed in the context of the magnetic flux quantization (see Fig. 4 and its discussion), as the particle makes one turn about the center, its wavefunction's phase kl may only change by $2\pi n$, with an arbitrary integer n (from $-\infty$ to $+\infty$),:

$$\psi_n(l + 2\pi R) = \psi_n(l) e^{2\pi i n}. \quad (3.128)$$

With eigenfunctions (127), this immediately gives condition gives $k 2\pi R = 2\pi n$. Thus, wavenumber k can take only quantized values $k_n = n/R$, so that the eigenfunctions should be indexed by n :

$$\psi_n = C_n \exp\left\{in \frac{l}{R}\right\}, \quad (3.129)$$

Planar rotator:
eigenfunctions

⁴⁷ This is a reasonable model for the confinement of light atoms, notably hydrogen, in some organic compounds.

and the energy spectrum is discrete:

Planar rotator:
eigenenergies

$$E_n = \frac{p_n^2}{2m} = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2}{2mR^2}. \quad (3.130)$$

So, while the free translation motion of a quantum particle is continuous, in the sense that its momentum has a continuous spectrum, its *rotation is quantized* – the most important fact, which has so many implications (including the existence of atoms, molecules, and hence us humans, and hence science including this course :-).

This simple model allows an exact analysis of external magnetic field effects on a quantum-confined motion of an electrically charged particle. Indeed, if this field is uniform and directed perpendicular to rotator's plane, it does not violate the axial symmetry of the system. According to Eq. (26), in this case we have to generalize Eq. (126) as

$$\hat{H} = \frac{1}{2m} \left(-i\hbar \mathbf{n}_\varphi \frac{\partial}{\partial l} - q\mathbf{A} \right)^2. \quad (3.131)$$

Here, in contrast to the gauge choice (44), which was so instrumental in the Landau level problem, it is now clearly beneficial to take the vector-potential in a manifestly axially-symmetric form $\mathbf{A} = A(\rho)\mathbf{n}_\varphi$, where $\mathbf{\rho} \equiv \{x, y\}$ is the 2D radius-vector. Using the well-known expression for curl in cylindrical coordinates,⁴⁸ we can readily check that the requirement $\nabla \times \mathbf{A} = \mathcal{B}\mathbf{n}_z$, with $\mathcal{B} = \text{const}$, is satisfied by the following function:

$$\mathbf{A} = \mathbf{n}_\varphi \frac{B\rho}{2}. \quad (3.132)$$

For the planar rotator, $\rho = R = \text{const}$, so that the stationary Schrödinger equation becomes

$$\frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial l} - q \frac{\mathcal{B}R}{2} \right)^2 \psi_n = E_n \psi_n. \quad (3.133)$$

A little bit surprisingly, this equation is still satisfied with the sine-wave eigenfunctions (127). Moreover, since the periodicity condition (128) is also unaffected by the applied magnetic field, we return to field-independent eigenfunctions (129). However, the field does affect the system's energy:

Planar rotator
in magnetic
field

$$E_n = \frac{1}{2m} \left(\frac{\hbar n}{R} - q \frac{\mathcal{B}R}{2} \right)^2 = \frac{\hbar^2}{2mR^2} \left(n - \frac{\Phi}{\Phi_0'} \right)^2, \quad (3.134)$$

where $\Phi \equiv \pi R^2 \mathcal{B}$ is the magnetic flux through the area limited by the particle's trajectory, and $\Phi_0' \equiv 2\pi\hbar/q$ is the “normal” magnetic flux quantum we have already met in the AB effect context – see Eq. (34) and its discussion. The field also changes the electric current of the particle in n -th state:

$$I_n = q \frac{\hbar}{2im} \left[\psi_n^* \left(\frac{\partial}{\partial l} - \frac{iqR\mathcal{B}}{2\hbar} \right) \psi_n - \text{c.c.} \right] = q \frac{\hbar}{mR} |C_n|^2 \left(n - \frac{\Phi}{\Phi_0'} \right). \quad (3.135)$$

Normalizing wavefunction (129) to have $W_n = 1$, we get $|C_n|^2 = 1/2\pi R$, so that Eq. (135) becomes

⁴⁸ See, e.g., MA Eq. (10.5).

$$I_n = I_0 \left(n - \frac{\Phi}{\Phi_0'} \right), \quad \text{with } I_0 \equiv \frac{\hbar q}{2\pi m R^2}. \quad (3.136)$$

Functions $E_n(\Phi)$ and $I_n(\Phi)$ are shown in Fig. 17. Note that since $\Phi_0' \propto 1/q$, for any sign of the particle's charge, $dI_n/d\Phi < 0$. It is easy to check that this means that the current is *diamagnetic*,⁴⁹ i.e. corresponds to the Lenz rule of the Faraday's electromagnetic induction: the field-induced current flows in such direction that its own magnetic field tries to compensate the external magnetic flux applied to the loop.

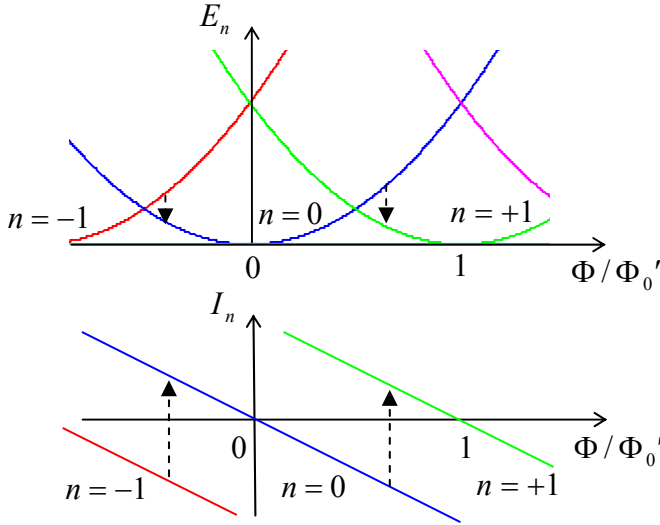


Fig. 3.17. Effect of magnetic field on a charged planar rotator. Dashed lines show possible inelastic transitions between metastable and ground states, due to weak interaction with environment, as the magnetic field is being increased.

This result may be interpreted as a different implementation of the AB effect.⁵⁰ In contrast to the two-slit interference experiment that was discussed in Sec. 1, in the situation shown in Fig. 17 the particle is not absorbed by the detector, but travels around the ring continuously. As a result, its wavefunction is *rigid*: due to the boundary condition (128), the topological quantum number n is discrete, and magnetic field cannot change the wavefunction gradually. In this sense, the system is similar to a superconducting loop - see Fig. 4 and its discussion. The difference between these systems is two-fold:

(i) For a single charged particle, in a macroscopic systems with practicable values of q , R , and m , the current scale I_0 is very small. For example, for $m = m_e$, $q = -e$, and $R = 1 \mu\text{m}$, Eq. (136) yields $I_0 \approx 3 \text{ pA}$.⁵¹ The contribution $LI \sim \mu_0 R I_0 \sim 10^{-24} \text{ Wb}$ of the current so small into the net magnetic flux is

⁴⁹ This effect, whose qualitative features remain the same for all 2D or 3D localized states (see Chapter 6 below), is frequently referred to as the *orbital diamagnetism*. In magnetic materials consisting of particles with uncompensated spins, this effect competes with another effect, *spin paramagnetism* - see, e.g., EM Sec. 5.5.

⁵⁰ It is straightforward to check that Eqs. (133) and hence (135) remain valid even if the magnetic field lines do not touch the particle's trajectory, and the field is localized well inside rotator's ring.

⁵¹ Such persistent, macroscopic diamagnetic currents in non-superconducting systems may be experimentally observed, for example, by measuring the weak magnetic field generated by electrons in a system of a large number ($\sim 10^7$) of similar conducting rings - see, e.g., L. Lévy *et al.*, *Phys. Rev. Lett.* **64**, 2074 (1990). Due to the

negligible in comparison with $\Phi_0' \sim 10^{-15}$ Wb, so that the quantization of n does not lead to the magnetic flux quantization.

(ii) As soon as the magnetic field raises the eigenstate energy E_n above that of another eigenstate $E_{n'}$, the former state becomes metastable, and weak interactions of the system with its environment (which are neglected in our simple model) may induce a quantum transition of the system to the lower-energy state, thus reducing the diamagnetic current's magnitude – see the dashed lines in Fig. 17. The flux quantization in superconductors is much more robust to such perturbations.⁵²

Now let us return, for one more time, to Eq. (129), and see what do they give for one more observable, particle's angular momentum

$$\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}, \quad (3.137)$$

In our current problem, vector $\mathbf{L}$ has just one component perpendicular to the rotator plane,

$$L_z = R p. \quad (3.138)$$

In classical mechanics, L_z of the rotator should be conserved (due to the absence of external torque), but can take arbitrary values. In quantum mechanics the situation changes: with $p = \hbar k$, our result $k_n = n/R$ may be rewritten as

$$L_z = (L_z)_n = R \hbar k_n = \hbar n. \quad (3.139)$$

Thus, the angular momentum is quantized: it may be only a multiple of the Planck constant $\hbar$ – confirming Bohr's guess – see Eq. (1.10). As we will see in Chapter 5, this result is very general (though may be modified by spin effects) and that wavefunctions (129) may be interpreted as eigenfunctions of the angular momentum operator.

In order to implement the planar rotator in our 3D world, we needed to provide rigid confinement of the particle both in the motion plane, and along radius ρ . Let us proceed to the more general problem when only the former confinement is strict, i.e. to a 2D particle moving in an arbitrary centrally-symmetric potential

$$U(\mathbf{p}) = U(\rho). \quad (3.140)$$

Using the well-known expression for the 2D Laplace operator in polar coordinates,⁵³ we may present the 2D stationary Schrödinger equation in the form

$$-\frac{\hbar^2}{2m} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} \right] \psi + U(\rho) \psi = E \psi. \quad (3.141)$$

Separating the radial and angular variables as⁵⁴

dephasing effects of electron scattering by phonons and other electrons, the effect's observation requires submicron samples and millikelvin temperatures.

⁵² Interrupting a superconducting ring with a weak link (Josephson junction), i.e. forming a SQUID, we may get the switching behavior similar to that shown with dashed arrows in Fig. 17 – see, e.g., EM Sec. 6.3.

⁵³ See, e.g., MA Eq. (10.3) with $\partial/\partial z = 0$.

⁵⁴ At this stage, I do not want to mark the particular solution (eigenfunction) ψ and corresponding eigenenergy E by any index, because we already may suspect that in a 2D problem the role of this index will be played by *two* integers – two quantum numbers.

$$\psi = \mathcal{R}(\rho)F(\varphi), \quad (3.142)$$

we get, after the division by ψ and multiplication by ρ^2 , the following equation:

$$-\frac{\hbar^2}{2m} \left[\frac{\rho}{\mathcal{R}} \frac{d}{d\rho} \left(\rho \frac{d\mathcal{R}}{d\rho} \right) + \frac{1}{F} \frac{d^2 F}{d\varphi^2} \right] + \rho^2 U(\rho) = \rho^2 E. \quad (3.143)$$

It is clear that the fraction $(d^2 F/d\varphi^2)/F$ should be a constant (because all other terms of the equation may be only functions of ρ alone), so that we get for function $F(\varphi)$ an ordinary differential equation,

$$\frac{d^2 F}{d\varphi^2} + \nu^2 F = 0, \quad (3.144)$$

where ν^2 is the variable separation constant. The fundamental solution of Eq. (144) is evidently $F \propto \exp\{\pm i\nu\varphi\}$. Now requiring, as we did for the planar rotator, the 2π periodicity of any observable, i.e.

$$F(\varphi + 2\pi) = F(\varphi)e^{2\pi i n}, \quad (3.145)$$

so that constant ν has to be integer (say, n), and we can write:⁵⁵

$$F_n = C_n e^{in\varphi}, \quad (3.146)$$

Plugging the resulting relation $(d^2 F/d\varphi^2)/F = -n^2$ into Eq. (143), we may rewrite is as

$$-\frac{\hbar^2}{2m} \left[\frac{1}{\rho\mathcal{R}} \frac{d}{d\rho} \left(\rho \frac{d\mathcal{R}}{d\rho} \right) - \frac{n^2}{\rho^2} \right] + U(\rho) = E. \quad (3.147)$$

The physical interpretation of this equation is that the full energy is a sum,

$$E = E_\rho + E_\varphi, \quad (3.148)$$

of the radial-motion part

$$E_\rho = -\frac{\hbar^2}{2m} \frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{d\mathcal{R}}{d\rho} \right) + U(\rho). \quad (3.149)$$

and the angular-motion part

$$E_\varphi = \frac{\hbar^2 n^2}{2m\rho^2}. \quad (3.150)$$

Now let us notice that a similar separation exists in classical mechanics,⁵⁶ because the total energy of a particle moving in a central field may be presented, within the plane of motion, as

$$E = \frac{m}{2} v^2 + U(\rho) = \frac{m}{2} (\dot{\rho}^2 + \rho \dot{\varphi}^2) + U(\rho) = E_\rho + E_\varphi, \quad (3.151)$$

where

⁵⁵ Noting that for the planar rotator (Fig. 16) $l/R = \varphi$, we can present Eq. (129) in a similar form. This is natural, because the rotator is just a particular case of our current problem - with a rigid confinement along axis ρ .

⁵⁶ See, e.g., CM Sec. 3.5.

$$E_\rho \equiv \frac{p_\rho^2}{2m} + U(\rho), \quad E_\varphi \equiv \frac{L_z^2}{2m\rho^2}. \quad (3.152)$$

The comparison of the latter relation with Eqs. (139) and (150) gives us grounds to suspect that the quantization rule $L_z = n\hbar$ may be valid for this problem as well, and may be in other cases as well. In Sec. 5.6, we will see that this is indeed the case.

Returning to Eq. (147), on the basis of our experience with 1D wave mechanics we may expect that this ordinary, linear, second-order differential equation should have (for a motion confined to a certain final region of its argument ρ), for any fixed n , a discrete energy spectrum described by some other integer quantum number (say, l). This means that eigenfunctions (142), and corresponding eigenenergies (148) should be indexed by two quantum numbers. Note, however, that since the radial function obeys equation (147), which already depends on n , function $\mathcal{R}(\rho)$ should carry both indices, so the variable separation is not so “clean” as it was for the rectangular quantum well. Normalizing the angular function to the full circle, $\Delta\varphi = 2\pi$, we may rewrite Eq. (142) as

$$\psi_{n,l} = \mathcal{R}_{n,l}(\rho)F_n(\varphi) = \frac{1}{(2\pi)^{1/2}} \mathcal{R}_{n,l}(\rho)e^{in\varphi}. \quad (3.153)$$

A good (and important) example of a solvable problem of this type is a free 2D particle whose motion is rigidly confined to a disk of radius R :

$$U(\rho) = \begin{cases} 0, & \text{for } 0 \leq \rho < R, \\ +\infty, & \text{for } R < \rho. \end{cases} \quad (3.154)$$

In this case, the solutions $\mathcal{R}_{n,l}(\rho)$ of Eq. (147) are proportional to the first-order Bessel functions $J_n(k_l\rho)$,⁵⁷ and the spectrum of possible values of parameter k_l should found the boundary condition $\mathcal{R}_{n,l}(R) = 0$. Let me leave the detailed solution and analysis of this problem for reader’s exercise.

3.6. Spherically-symmetric systems: Brute force approach

Now let us address the (mathematically more involved) case of 3D motion, with spherically-symmetric potential

$$U(\mathbf{r}) = U(r). \quad (3.155)$$

Let me start, again, with a rigid rotator - now a *spherical rotator*, i.e. a particle confined to move on the surface of a sphere of radius R . It has 2 degrees of freedom, because any position on the spherical surface is completely described by two coordinates – say, the polar angle θ and the azimuthal angle φ . In this case, the kinetic energy we need to consider is limited to its angular part, so that in the Laplace operator in spherical coordinates⁵⁸ we may keep only those parts, with fixed $r = R$. Then the stationary Schrödinger equation becomes

⁵⁷ A short summary of properties of these function, plus a few plots and a useful table of values, may be found in EM Sec. 2.4. For more on of Bessel functions, see the literature recommended in MA Sec. 16(ii).

⁵⁸ See, e.g., MA Eq. (10.9).

$$-\frac{\hbar^2}{2mR^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \psi = E \psi. \quad (3.156)$$

(Again, I abstain from attaching any indices to ψ and E for the time being.) With the usual variable separation assumption,

$$\psi = \Theta(\theta)F(\varphi), \quad (3.157)$$

Eq. (156), with all terms multiplied by $\sin^2 \theta / \Theta F$, yields

$$-\frac{\hbar^2}{2mR^2} \left[\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{F} \frac{d^2 F}{d\varphi^2} \right] = E \sin^2 \theta. \quad (3.158)$$

Just as in Eq. (143), fraction $(d^2 F/d\varphi^2)/F$ may be a function of φ only, and hence has to be constant, giving for it an equation similar to Eq. (144). So, the azimuthal functions are just the sine waves (146) again, and we can use the same periodicity condition (145) to write them in the normalized form⁵⁹

$$F_m(\varphi) = \frac{1}{(2\pi)^{1/2}} e^{im\varphi}. \quad (3.159)$$

With that, fraction $(d^2 F/d\varphi^2)/F$ equals $(-m^2)$, and Eq. (158), after multiplication by $\Theta/\sin^2 \theta$, is reduced to the following ordinary, linear differential equation for function $\Theta(\theta)$:

$$-\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} \Theta = \varepsilon \Theta, \quad \text{with } \varepsilon \equiv E / \left(\frac{\hbar^2}{2mR^2} \right), \quad (3.160)$$

It is convenient to recast it into an equation for a new variable $P(\xi) \equiv \Theta(\theta)$, with $\xi \equiv \cos \theta$:

$$\frac{d}{d\xi} \left[(1-\xi^2) \frac{dP}{d\xi} \right] + \left[l(l+1) - \frac{m^2}{1-\xi^2} \right] P = 0, \quad (3.161)$$

where a new notation for the normalized energy is introduced: $l(l+1) \equiv \varepsilon$. The motivation for such notation is that, according to a mathematical analysis,⁶⁰ Eq. (161) with integer m , has solutions only if parameter l is integer: $l = 0, 1, 2, \dots$, and only if that integer is not smaller than $|m|$, i.e. if

$$-l \leq m \leq +l. \quad (3.162)$$

This immediately gives the following energy spectrum of the spherical rotator:

$$E_l = \frac{\hbar^2 l(l+1)}{2mR^2}, \quad (3.163)$$

Energy
spectrum
of spherical
rotator

⁵⁹ Here, rather regrettably, I had to replace the notation of the integer from n to m , in order to comply with the generally accepted convention for this so-called *magnetic quantum number*. Let me hope that the difference between this integer and particle's mass is absolutely clear from the context.

⁶⁰ It was carried out by A.-M. Legendre (1752-1833). Just as a historic note: besides many original mathematical results, Dr. Legendre has authored the famous textbook *Éléments de Géométrie* which dominated teaching geometry through the 19th century.

so that the only effect of the magnetic quantum number m here is imposing the restriction (162) on the *orbital quantum number* l . This means, in particular, that each of energy level (163) corresponds to $(2l + 1)$ different values of m , i.e. is $(2l + 1)$ -degenerate.

To understand the physics of this degeneracy, we need to explore the corresponding eigenfunctions of Eq. (161). They are naturally numbered by two integers, m and l , and are called the *associated Legendre functions* P_l^m . For the particular, simplest case $m = 0$, these functions are just (*Legendre*) *polynomials* $P_l(\xi) \equiv P_l^0(\xi)$, which may be either defined as the solutions of the *Legendre equation* following from Eq. (161) at $m = 0$:

Legendre
equation

$$\frac{d}{d\xi} \left[(1 - \xi^2) \frac{d}{d\xi} P \right] + l(l+1)P = 0, \quad (3.164)$$

or calculated explicitly from the following *Rodrigues formula*:⁶¹

Rodrigues
formula for
Legendre
polynomials

$$P_l(\xi) = \frac{1}{2^l l!} \frac{d^l}{d\xi^l} (\xi^2 - 1)^l, \quad l = 0, 1, 2, \dots \quad (3.165)$$

Using this formula, it easy to spell out a few lowest Legendre polynomials:

$$P_0(\xi) = 1, \quad P_1(\xi) = \xi, \quad P_2(\xi) = \frac{1}{2}(3\xi^2 - 1), \quad P_3(\xi) = \frac{1}{2}(5\xi^3 - 3\xi), \dots, \quad (3.166)$$

though such expressions become more and more bulky as l is increased. As Fig. 18 shows, as argument ξ is decreased, all these functions start in one point, $P_l(+1) = +1$, and end up either in the same point or in the opposite point: $P_l(-1) = (-1)^l$. On the way between these two end points, the l^{th} polynomial crosses the horizontal axis exactly l times, i.e. has l roots.⁶² It may be shown that on the segment $[-1, +1]$, the Lagrange polynomials form a full orthogonal set of functions, with the following normalization rule:

$$\int_{-1}^{+1} P_l(\xi) P_{l'}(\xi) d\xi = \frac{2}{2l+1} \delta_{ll'}. \quad (3.167)$$

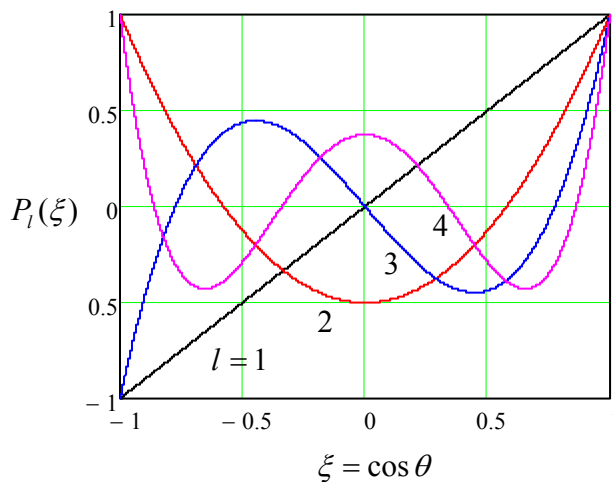


Fig. 3.18. A few lowest Legendre polynomials.

⁶¹ Derived independently by B. O. Rodrigues in 1816, J. Ivory in 1824, and C. Jacobi in 1827.

⁶² In this behavior, we readily recognize the standing wave pattern typical for all 1D eigenproblems – cf. Fig. 1.7. The quantitative deviation from the sinusoidal waveform is due to the different metric of the sphere.

For $m > 0$, the associated Legendre functions may be expressed via the Legendre polynomials (165) using the following formula, which reminds Eq. (165):

$$P_l^m(\xi) = (-1)^m (1 - \xi^2)^{m/2} \frac{d^m}{d\xi^m} P_l(\xi), \quad (3.168)$$

while if the index m is negative, the following simple relation may be used:

$$P_l^{-m}(\xi) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(\xi). \quad (3.169)$$

Associated
Legendre
functions

On the segment $\xi = [-1, +1]$, each set of the associated Legendre functions with fixed index m forms a full orthogonal set, with the normalization relation,

$$\int_{-1}^{+1} P_l^m(\xi) P_{l'}^m(\xi) d\xi = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{ll'}, \quad (3.170)$$

which is evidently a generalization of Eq. (167) for arbitrary m .

Since the difference between angles θ and φ is to some extent artificial (caused by the arbitrary direction of the polar axis), physicists prefer to use not the functions $\Theta(\theta) \propto P_l^m(\cos\theta)$ and $F_m(\varphi) \propto \exp\{im\varphi\}$ separately, but their products (157), which are called *spherical harmonics*:

$$Y_l^m(\theta, \varphi) = \left[\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos\theta) e^{im\varphi}. \quad (3.171)$$

Spherical
harmonics

The specific coefficient in Eq. (171) is chosen in a way to simplify the following two relations: the equation for negative m ,

$$Y_l^{-m}(\theta, \varphi) = (-1)^m [Y_l^m(\theta, \varphi)]^*, \quad (3.172)$$

and the normalization relation

$$\oint Y_l^m(\theta, \varphi) [Y_{l'}^{m'}(\theta, \varphi)]^* d\Omega = \delta_{ll'} \delta_{mm'}, \quad (3.173)$$

with integration over the whole solid angle 4π . The last relation shows that the spherical harmonics form an orthonormal set of functions. This set is also full, so that any function defined on a sphere may be uniquely presented as a linear combination of Y_l^m .

Despite a somewhat intimidating formulas given above, they yield rather simple expressions for the lowest spherical harmonics:

$$l = 0: \quad Y_0^0 = (1/4\pi)^{1/2}, \quad (3.174)$$

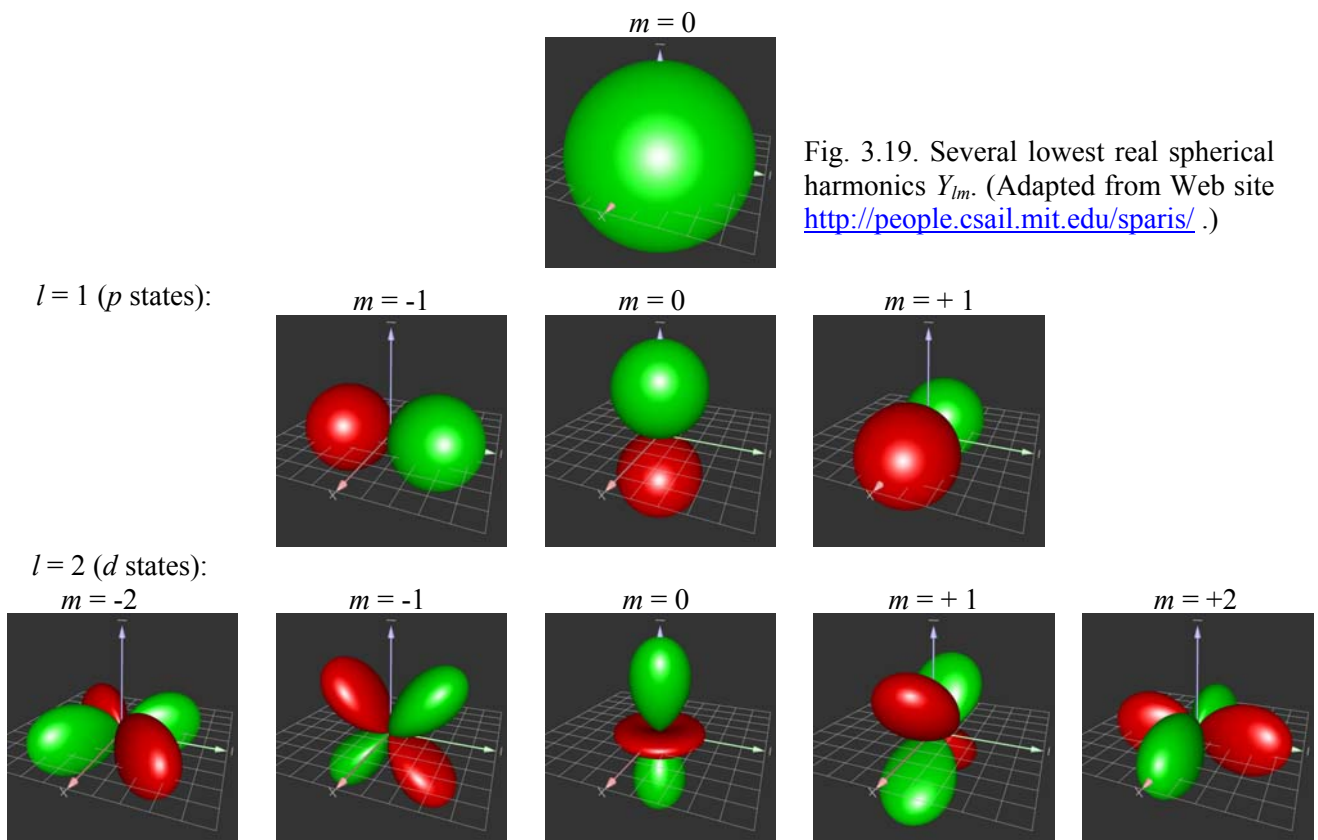
$$l = 1: \quad \begin{cases} Y_1^1 = -(3/8\pi)^{1/2} \sin\theta e^{i\varphi}, \\ Y_1^0 = (3/4\pi)^{1/2} \cos\theta, \\ Y_1^{-1} = +(3/8\pi)^{1/2} \sin\theta e^{-i\varphi}, \end{cases} \quad (3.175)$$

$$l = 2 : \begin{cases} Y_2^2 = +(15/32\pi)^{1/2} \sin^2 \theta e^{2i\varphi}, \\ Y_2^1 = -(15/8\pi)^{1/2} \sin \theta \cos \theta e^{i\varphi}, \\ Y_2^0 = (3/16\pi)^{1/2} (3 \cos^2 \theta - 1), \\ Y_2^{-1} = +(15/8\pi)^{1/2} \sin \theta \cos \theta e^{-i\varphi}, \\ Y_2^{-2} = -(15/32\pi)^{1/2} \sin^2 \theta e^{-2i\varphi}. \end{cases} \quad (3.176)$$

It is important to understand the symmetry of these functions. Since spherical functions with $m \neq 0$ are complex, the most popular way of their graphical representation is first to form their real combinations corresponding to two opposite values of m ,⁶³

$$Y_{lm} \equiv \frac{1}{\sqrt{2}} \left[Y_l^{|m|} + \text{sgn}(m)(-1)^m Y_l^{-|m|} \right] \propto \begin{cases} \cos m\varphi, & \text{for } m > 0, \\ \sin m\varphi, & \text{for } m < 0, \end{cases} \quad (3.177)$$

(for $m = 0$, $Y_{l0} \equiv Y_l^0$), and then plot the magnitude of these combinations in spherical coordinates as the distance from the origin, while using two colors to show their sign – see Fig. 19.



⁶³ Such real functions Y_{lm} , which also form the full set of orthonormal eigenfunctions and are frequently called the *real spherical harmonics*, are more convenient than the complex functions Y_l^m for several applications, especially when the variables of interest are real by definition.

Let us starting from the simplest case $l = 0$. According to Eq. (162), there could be only one such s state,⁶⁴ with $m = 0$. The spherical harmonic corresponding to that state is just a constant, so that the wavefunction is uniformly distributed over the sphere. Since the functions does not have gradient in any direction, the kinetic energy (163) of the particle equals is zero.

For $l = 1$, there could be 3 different p states, with $m = -1, 0$, and $+1$. As the second row in Fig. 19 shows, these states are essentially identical in structure, and are just differently oriented in space, thus explaining the 3-fold degeneracy of the kinetic energy – see Eq. (163). This is not quite true for 5 different d states ($l = 2$), shown in the bottom row of Fig. 19, as well as states with higher l : despite their equal energies, they differ not only by their special orientation. The states with $m = 0$ have gradient only in the θ direction, while the states with the ultimate values of m ($m = \pm l$) change only gradually (as $\sin^l \theta$) in the polar direction, while oscillating in the azimuthal direction. The states with intermediate values of m provide a crossover between these two extremes, oscillating in both directions, stronger and stronger in the direction of φ as $|m|$ is increased. Still, the magnetic quantum number, surprisingly, does not affect the energy for any l . Another surprising feature of the spherical harmonics follows from the comparison of Eq. (163) with the second of classical relations (152). These expressions coincide if we interpret constant

$$L^2 \equiv \hbar^2 l(l+1), \quad (3.178)$$

as the value of the full angular momentum squared $L^2 = |\mathbf{L}|^2$ (including its both θ and φ components) in the eigenstate with eigenfunction Y_l^m . On the other hand, the structure of the azimuthal component $F(\varphi)$ of the wavefunction is exactly the same as in 2D axially-symmetric problems, suggesting that Eq. (139) still gives correct values (in our new notation, $L_z = m\hbar$) for the z -component of the angular momentum. If this is so, why for any state with $l > 0$, $(L_z)^2 = m^2 \hbar^2 \leq l^2 \hbar^2$ is less than $L^2 = l(l+1)\hbar^2$? In other words, what prevents the angular momentum vector to be fully aligned with axis z ?

Besides that issue, though the above analysis of the spherical rotator is formally (mathematically) complete, it is as unsatisfactory on the physics level as the harmonic oscillator analysis in Sec. 2.6. In particular, it does not explain the meaning of the extremely simple relations for eigenvalues of energy and angular momentum on the backdrop of rather complicated wavefunctions.

We will obtain natural answers to all these questions and concerns in Sec. 5.6, but now let us complete our survey of wave mechanics by extending it to 3D motion in an *arbitrary* spherically-symmetric potential (155). In this case we have to use the full form of the Laplace operator in spherical coordinates. The variable separation procedure is an evident generalization of what we have done before, with the particular solution

$$\psi = \mathcal{R}(\rho)\Theta(\theta)F(\varphi), \quad (3.179)$$

whose substitution into the stationary Schrödinger equation yields

$$-\frac{\hbar^2}{2mr^2} \left[\frac{1}{\mathcal{R}} \frac{d}{dr} \left(r^2 \frac{d\mathcal{R}}{dr} \right) + \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{1}{F} \frac{d^2 F}{d\varphi^2} \right] + U(r) = E. \quad (3.180)$$

⁶⁴ The letter names for states with different values of l stem from the history of optical spectroscopy - for example, letter “s”, used for $l = 0$, originally denoted the “sharp” optical line series, etc. The sequence of the letters is as follows: s, p, d, f, g, h , and further in the alphabetical order.

It is evident that the angular part (the two last terms in square brackets) separates from the radial part, and for the former part we get Eq. (156) again, with the only change, $R \rightarrow r$. This change does not affect the fact that the eigenfunctions of that equation are the spherical harmonics (171), and the angular eigenenergy is given by Eq. (163), again with the replacement $R \rightarrow r$. This means that for the radial function, Eq. (180) gives the following equation,

$$-\frac{\hbar^2}{2mr^2} \left[\frac{1}{\mathcal{R}} \frac{d}{dr} \left(r^2 \frac{d\mathcal{R}}{dr} \right) - l(l+1) \right] + U(r) = E. \quad (3.181)$$

Note that no information about the magnetic quantum number m has not crept into the radial equation (besides establishing the limitation (162) for possible values of l), so that this equation depends only on the latter quantum number.

The radial equation becomes rather simple for $U(r) = 0$, and may be used, for example, to solve the eigenproblem for the free 3D motion of a particle inside the sphere of radius R . Leaving that problem for the reader's exercise, I will proceed to the most important *Bohr atom problem*, i.e. of motion in the so-called *attractive Coulomb potential*⁶⁵

$$U(r) = -\frac{C}{r}, \quad \text{with } C > 0. \quad (3.182)$$

The natural scales of r and E are, respectively,⁶⁶

$$r_0 \equiv \frac{\hbar^2}{mC} \quad \text{and} \quad E_0 \equiv \frac{\hbar^2}{mr_0^2} \equiv m \left(\frac{C}{\hbar} \right)^2. \quad (3.183)$$

In the normalized units $\varepsilon \equiv E/E_0$ and $\xi \equiv r/r_0$, Eq. (181) looks simpler,

$$\frac{d^2 \mathcal{R}}{d\xi^2} + \frac{2}{\xi} \frac{d\mathcal{R}}{d\xi} - l(l+1)\mathcal{R} + 2 \left(\varepsilon + \frac{1}{\xi} \right) \mathcal{R} = 0, \quad (3.184)$$

but unfortunately its eigenfunctions may be called elementary only in the most generous meaning of the word. With the adequate normalization,

$$\int_0^\infty \mathcal{R}_{n,l} \mathcal{R}_{n',l} r^2 dr = \delta_{nn'}, \quad (3.185)$$

these (mutually orthogonal) functions may be presented as

⁶⁵ Historically, the solution of this problem in 1928, that reproduced the main result (1.8)-(1.9) of the “old” quantum theory developed by N. Bohr in 1912, without its restrictive assumptions, was the decisive step for the general acceptance of Schrödinger's wave mechanics.

⁶⁶ These two scales are obtained from relations $E_0 \equiv \hbar^2/mr_0^2 \equiv C/r_0$, i.e. from the equality of the natural scales of the potential and kinetic energies, dropping all numerical coefficients. For the most important case of the hydrogen atom, $C = e^2/4\pi\epsilon_0$, these scales are reduced, respectively, to the Bohr radius r_B (1.13) and the Hartree energy E_H (1.9). Note also that for a *hydrogen-like atom* (or rather ion), with $C = Z(e^2/4\pi\epsilon_0)$, these two key parameters are rescaled as $r_0 = r_B/Z$, $E_0 = Z^2 E_H$.

$$\mathcal{R}_{n,l}(r) = - \left\{ \left(\frac{2}{nr_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} \exp \left\{ -\frac{r}{nr_0} \right\} \left(\frac{2r}{nr_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{nr_0} \right). \quad (3.186)$$

Bohr
atom's
radial
functions

Here $L_p^q(\xi)$ are the so-called *associated Laguerre polynomials*, which may be calculated as

$$L_p^q(\xi) = (-1)^q \frac{d^q}{d\xi^q} L_{p+q}(\xi). \quad (3.187)$$

Associated
Laguerre
polynomials

from *simple Laguerre polynomials* $L_p(\xi) \equiv L_p^0(\xi)$.⁶⁷ In turn, the easiest way to obtain $L_p(\xi)$ is to use the following *Rodrigues formula*:⁶⁸

$$L_p(\xi) = e^\xi \frac{d^p}{d\xi^p} \left(\xi^p e^{-\xi} \right). \quad (3.188)$$

Rodrigues
formula for
Laguerre
polynomials

Notice that in contrast with the associated Legendre *functions* P_l^m participating in spherical harmonics, L_p^q are just *polynomials*, and those with small indices p and q are indeed simple.

Returning to Eq. (186), we see that the natural quantization of the radial equation (184) has brought us a new quantum number (integer) n . In order to understand its range, we should notice that according to Eq. (188), the highest power of terms in polynomial L_{p+q} is $(p+q)$, and hence, according to Eq. (187), that of L_p^q is p , so that of the highest power in the polynomial participating in Eq. (186) is $(n-l-1)$. Since the power cannot be negative (to avoid the unphysical divergence of wavefunctions at $r \rightarrow 0$), the radial quantum number n has to obey the restriction $n \geq l+1$. Since l , as we already know, may take values $l = 0, 1, 2, \dots$, we may conclude that n may only take values

$$n = 1, 2, \dots \quad (3.189)$$

What makes this relation important is the following, most surprising result of the theory: the eigenenergies corresponding to wavefunctions (179), which are indexed with 3 quantum numbers:

$$\psi_{n,l,m} = \mathcal{R}_{n,l}(r) Y_l^m(\theta, \varphi), \quad (3.190)$$

depend only on n and agree with Bohr's formula (1.8):

$$E_n = -\frac{E_0}{2n^2} = -\frac{1}{2n^2} m \left(\frac{C}{\hbar} \right)^2. \quad (3.191)$$

Because of this reason, n is usually called the *principal quantum number*, and the above relation between it and “more subordinate” l is rewritten as

$$l \leq n-1. \quad (3.192)$$

Together with inequality (162), this gives us the most important hierarchy of the 3 quantum numbers involved in the problem:

$$1 \leq n \leq \infty \Rightarrow 0 \leq l \leq n-1 \Rightarrow -l \leq m \leq +l, \quad (3.193)$$

Bohr
atom's
quantum
numbers

⁶⁷ In Eqs. (187)-(188), p and q are non-negative integers, with no relation whatsoever to particle's momentum or electric charge. Sorry for this notation, but it is absolutely common, and can hardly result in any confusion.

⁶⁸ Named after the same B. O. Rodrigues, and belonging to the same class as his another key result, Eq. (165).

Taking into account the $(2l+1)$ -degeneracy related to the magnetic number m , and using the well-known formula for the arithmetic progression,⁶⁹ we see that each energy level (191) has the following *orbital degeneracy*:

$$g = \sum_{l=0}^{n-1} (2l+1) = 2 \sum_{l=0}^{n-1} l - \sum_{l=0}^{n-1} 1 = 2 \frac{n(n-1)}{2} - n = n^2. \quad (3.194)$$

Due to its importance for applications, let us spell out the quantum number hierarchy of a few lowest-energy states, using the traditional notation in which the value of n is followed by the letter that denotes the value of l :

$$n = 1: \quad l = 0 \quad (\text{one } 1s \text{ state}) \quad m = 0. \quad (3.195)$$

$$n = 2: \quad l = 0 \quad (\text{one } 2s \text{ state}) \quad m = 0, \\ l = 1 \quad (\text{three } 2p \text{ states}) \quad m = 0, \pm 1. \quad (3.196)$$

$$n = 3: \quad l = 0 \quad (\text{one } 3s \text{ state}) \quad m = 0, \\ l = 1 \quad (\text{three } 3p \text{ states}) \quad m = 0, \pm 1, \\ l = 2 \quad (\text{five } 3d \text{ states}) \quad m = 0, \pm 1, \pm 2. \quad (3.197)$$

Figure 20 shows plots of the radial functions (186) of the listed states. The most important of them is of course the ground ($1s$) state with $n = 1$ and hence $E = -E_0/2$, whose radial function (186) is just

Ground
state's
radial
function

$$\mathcal{R}_{1,0}(r) = \frac{2}{r_0^{3/2}} e^{-r/r_0}, \quad (3.198)$$

and the angular distribution is uniform - see Eq. (174). The gap between the ground energy and the energy $E = -E_0/8$ of the lowest excited states (with $n = 2$) in a hydrogen atom (in which $E_0 = E_H \approx 27.2$ eV) is as large as ~ 10 eV, so that their thermal excitation requires temperatures as high as $\sim 10^5$ K, and the overwhelming part of all hydrogen atoms in the visible Universe are in their ground state. Since atomic hydrogen makes up about 75% of the “normal” matter, we are very fortunate that such simple formulas as Eqs. (174) and (198) describe the atomic states most frequently met in Mother Nature!⁷⁰

The radial functions of the next states, $2s$ and $2p$, are also not too complex:

$$\mathcal{R}_{2,0}(r) = \frac{1}{(2r_0)^{3/2}} \left(2 - \frac{r}{r_0} \right) e^{-r/2r_0}, \quad \mathcal{R}_{2,1}(r) = \frac{1}{(2r_0)^{3/2}} \frac{r}{3^{1/2} r_0} e^{-r/2r_0}. \quad (3.199)$$

(Note again that the former of these states ($2s$) can only have a uniform angular distribution, while three $2p$ states have different values of $m = 0, \pm 1$, and hence have different angular distributions – see Eq. (175) and the second row of Fig. 19.) The most important trend here is a larger radius of decay of the exponent ($2r_0$ for $n = 2$ instead of r_0 for $n = 1$), and hence the radial extension of the states. This trend is confirmed by the following general formula:⁷¹

⁶⁹ See, e.g., MA Eq. (2.5a).

⁷⁰ Forgetting for a minute about such new “dark clouds” on the horizon of the modern physics as the hypothetical dark matter and dark energy.

⁷¹ Note that even at the largest value of l , equal to $(n-1)$, term $l(l+1)$ in Eq. (200) cannot compensate term $3n^2$.

$$\langle r \rangle_{n,l} = \frac{r_0}{2} [3n^2 - l(l+1)]. \quad (3.200)$$

The second important trend is that at fixed n , the orbital quantum number l determines how fast does the wavefunction change with r near the origin, and how much it oscillates in the radial direction at larger r . For example, the $2s$ eigenfunction $\mathcal{R}_{2,0}(r)$ is nonvanishing at $r = 0$, and makes one “wiggle” (has one root) in the radial direction, while eigenfunctions $2p$ equal zero at $r = 0$, and do not oscillate at all in the radial direction. Instead, those wavefunctions always oscillate as functions of some angle – see the second row of Fig. 19. The same trend is clearly visible for $n = 3$ (see Fig. 20), and continues for the higher values of n .

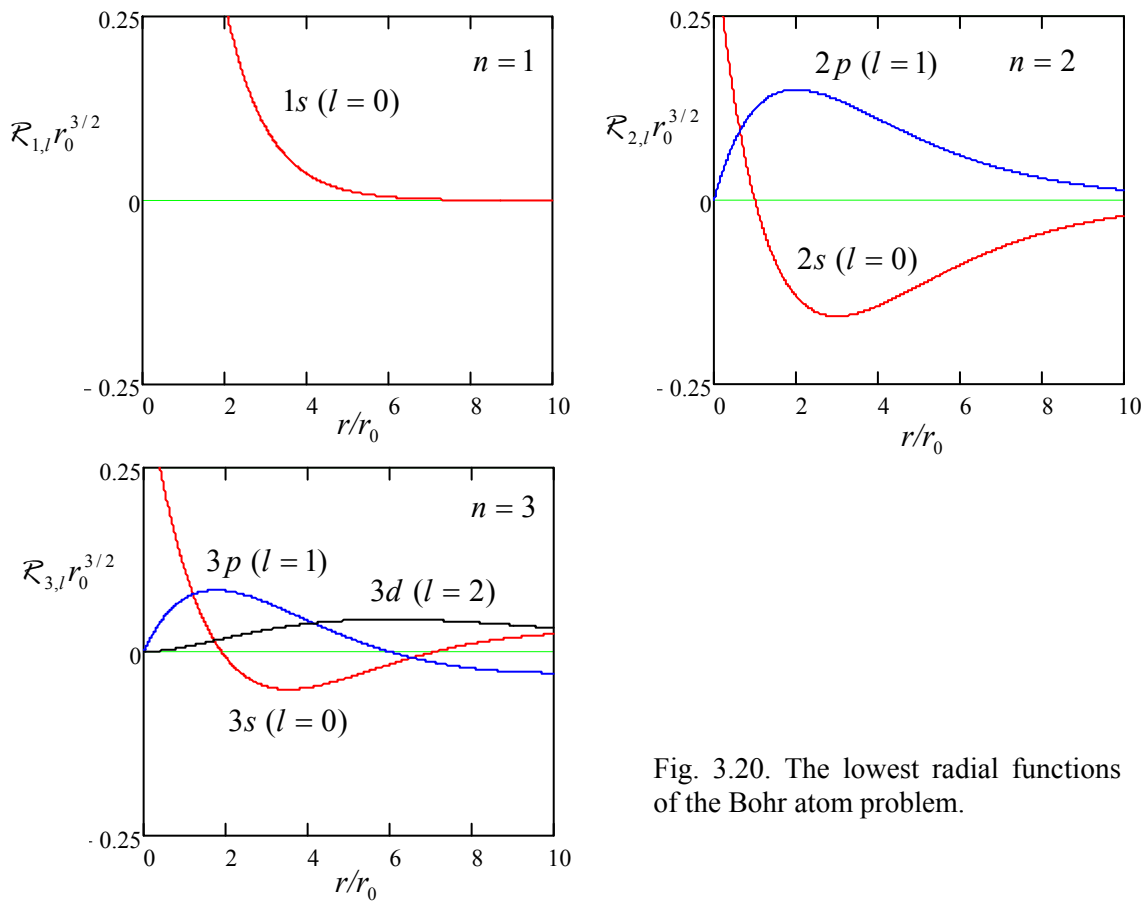


Fig. 3.20. The lowest radial functions of the Bohr atom problem.

The interpretation of these results is that the states with $l = l_{\max} = n - 1$ may be viewed as analogs of the circular motion of a particle in a plane whose orientation defines the quantum number m , with an almost fixed radius $r \approx r_0(n^2 \pm n)$. On the other hand, the best classical image of an s -state ($l = 0$) is the purely radial motion of the particle to and from the attracting center. (The latter image is especially imperfect, because the motion would need to happen simultaneously in all radial directions.) The classical language becomes reasonable only for the so-called *Rydberg states*, with $n \gg 1$, whose linear superpositions may be used to compose wave packets closely following the classical, circular or elliptic trajectories of the particle – just as was discussed in Sec. 2.2 for the free 1D motion.

Besides Eq. (200), mathematics gives us several other simple relations for the radial functions $\mathcal{R}_{n,l}$ (and, since the spherical harmonics are normalized to 1, for the eigenfunctions as the whole), including those that we will use later in the course:⁷²

$$\left\langle \frac{1}{r} \right\rangle_{n,l} = \frac{1}{n^2 r_0}, \quad \left\langle \frac{1}{r^2} \right\rangle_{n,l} = \frac{1}{n^3 (l+1/2) r_0^2}, \quad \left\langle \frac{1}{r^3} \right\rangle_{n,l} = \frac{1}{n^3 l(l+1/2)(l+1) r_0^3}. \quad (3.201)$$

In particular, the first of them means that for *any* eigenfunction $\psi_{n,l,m}$, with all its complicated radial and angular dependencies, there is a simple relation between the potential and full energies:

$$\langle U \rangle_{n,l} = -C \left\langle \frac{1}{r} \right\rangle_{n,l} = -\frac{C}{n^2 r_0} = -\frac{E_0}{n^2} = 2E_n, \quad (3.202)$$

so that the average kinetic energy of the particle, $\langle T \rangle_{n,l} = E_n - \langle U \rangle_{n,l}$, is equal to $|E_n| > 0$.

These simple results are in a sharp contrast with the rather complicated expressions for the eigenfunctions, and motivate a search for more general methods of quantum mechanics, which would replace or at least complement our brute-force (wave-mechanics) approach, to reveal their real nature. Such an approach will be the main topic of the next chapter.

3.7. Atoms

Before proceeding to that chapter, let me show that, rather strikingly, the classification of quantum numbers in the simple potential well (182), carried out in the last section, together with very modest borrowings from the further theory, allows an semi-quantitative explanation of the whole system of chemical elements. The “only” two additions we need are the following facts:

- (i) due to interaction with relatively low-temperature environments, atoms tend to relax into their lowest-energy state, and
- (ii) due to the Pauli principle (valid for electrons as Fermi particles), each *orbital eigenstate* discussed above can be occupied with 2 electrons with opposite spins.

Of course, atomic electrons do interact, so that their quantitative description requires quantum mechanics of multiparticle systems, which is rather complex. (Its main concepts will be discussed in Chapter 8.) However, the lion’s share of this interaction reduces to simple electrostatic *screening*, i.e. the partial compensation of the electric charge of the atomic nucleus, as felt by a particular electron, by other electrons of the atom. This screening changes the qualitative results (such as the energy scale) dramatically; however, the quantum number hierarchy, and hence their classification, is not affected.

The system of atoms is most often presented as the famous *periodic table of chemical elements*,⁷³ whose simple version is shown in Fig. 21, while Fig. 22 presents a sequential list of the elements with their electron configurations. The numbers in table’s cells (and the first column in the list) are the

⁷² The first of these relations may be also readily proved using the Heller-Feynman theorem (see Chapter 1); this proof is left for reader’s exercise. Note also that the last of the expressions diverges at $l = 0$, in particular in the ground state of the system (with $n = 1, l = 0$).

⁷³ Also called the *Mendeleev table*, after D. Mendeleev who put forward the concept of the periodicity of chemical element properties as functions of Z phenomenologically in 1869. (The explanation of the periodicity had to wait for 60 more years until the quantum mechanics formulation in the late 1920s.)

atomic numbers Z , which physically are the numbers of protons in the atomic nucleus, and hence the numbers of electrons in the electrically neutral atom. The electron configuration in Fig. 22 follows the convention already used in Eqs. (195)-(197), with the additional upper index showing the number of electrons with the indicated values of quantum numbers n and l .

The lightest atom, with $Z = 1$, is hydrogen (chemical symbol H) – the only atom for each the theory discussed in Sec. 6 is quantitatively correct.⁷⁴ According to Eq. (191), the $1s$ ground state of its only electron corresponds to quantum numbers $n = 1$, $l = 0$, and $m = 0$ – see Eq. (196). In most versions of the periodic table, the cell of H is placed in the top left corner. In the next atom, helium (He, $Z = 2$), the same orbital quantum state ($1s$) is filled with two electrons with different spins.⁷⁵ Note that due to the twice higher electric charge of the nucleus, i.e. the twice higher value of constant C in Eq. (182), resulting in a 4-fold increase of constant E_0 (183), the binding energy of each electron is crudely 4 times higher than that of the hydrogen atom – though the electron interaction decreases it by about 25% – see Sec. 7.2. This is why taking one electron away (i.e. *positive ionization*) of the helium atom requires a very high energy, 23.4 eV, which is not available in usual chemical reactions. On the other hand, a neutral helium atom cannot bind one more electron (i.e. form a *negative ion*) either. As a result, helium, and all other elements with fully completed electron *shells* (sets of states with eigenenergies well separated from higher energy levels) is a chemically inert *noble gas*, thus starting the whole right-most column of the periodic table, committed to such elements.

1 H	Property legend:																2 He
3 Li	4 Be	alkali metals			transition metals			metalloids			5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg	alkali-earth metals			nonmetals			halogens			13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
		rare-earth metals			other metals			noble gases									
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Lanthanides:

Actinides:

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 Lr

Fig. 21. The periodic table of elements, showing their atomic numbers, as well as their basic physical/chemical properties at the so-called *ambient* (meaning usual laboratory) *conditions*.

⁷⁴ Besides very small “fine-structure” corrections – to be discussed in Chapters 6 and 9.

⁷⁵ As will be discussed in detail in Chapter 8, electrons of the same atom are actually *indistinguishable*, and their quantum states are not independent, and frequently *entangled*. These factors are important for several properties of helium atoms (and heavier elements as well), especially for their response to external fields. However, for the atom classification purposes, they are not crucial.

Atomic number	Atomic symbol	Electron states	Atomic number	Atomic symbol	Electron states	Atomic number	Atomic symbol	Electron states
Period 1			Period 5			Period 7		
1	H	$1s^1$	37	Rb	[Kr] shell, plus: $5s^1$	77	Ir	$4f^{14}5d^76s^2$
2	He	$1s^2$	38	Sr	$5s^2$	78	Pt	$4f^{14}5d^96s^1$
Period 2			39	Y	$4d^15s^2$	79	Au	$4f^{14}5d^{10}6s^1$
3	Li	[He] shell, plus: $2s^1$	40	Zr	$4d^25s^2$	80	Hg	$4f^{14}5d^{10}6s^2$
4	Be	$2s^2$	41	Nb	$4d^45s^1$	81	Tl	$4f^{14}5d^{10}6s^26p^1$
5	B	$2s^22p^1$	42	Mo	$4d^55s^1$	82	Pb	$4f^{14}5d^{10}6s^26p^2$
6	C	$2s^22p^2$	43	Tc	$4d^65s^1$	83	Bi	$4f^{14}5d^{10}6s^26p^3$
7	N	$2s^22p^3$	44	Ru	$4d^75s^1$	84	Po	$4f^{14}5d^{10}6s^26p^4$
8	O	$2s^22p^4$	45	Rh	$4d^85s^1$	85	At	$4f^{14}5d^{10}6s^26p^5$
9	F	$2s^22p^5$	46	Pd	$4d^{10}$	86	Rn	$4f^{14}5d^{10}6s^26p^6$
10	Ne	$2s^22p^6$	47	Ag	$4d^{10}5s^1$	Period 7		
Period 3			48	Cd	$4d^{10}5s^2$	87	Fr	[Rn] shell, plus: $7s^1$
11	Na	[Ne] shell, plus: $3s^1$	49	In	$4d^{10}5s^25p^1$	88	Ra	$7s^2$
12	Mg	$3s^2$	50	Sn	$4d^{10}5s^25p^2$	89	Ac	$6d^17s^2$
13	Al	$3s^23p^1$	51	Sb	$4d^{10}5s^25p^3$	90	Th	$6d^27s^2$
14	Si	$3s^23p^2$	52	Te	$4d^{10}5s^25p^4$	91	Pa	$5f^26d^17s^2$
15	P	$3s^23p^3$	53	I	$4d^{10}5s^25p^5$	92	U	$5f^36d^17s^2$
16	S	$3s^23p^4$	54	Xe	$4d^{10}5s^25p^6$	93	Np	$5f^46d^17s^2$
17	Cl	$3s^23p^5$	Period 6			94	Pu	$5f^67s^2$
18	Ar	$3s^23p^6$	Period 6			95	Am	$5f^77s^2$
Period 4			55	Cs	[Xe] shell, plus: $6s^1$	96	Cm	$5f^76d^17s^2$
19	K	[Ar] shell, plus: $4s^1$	56	Ba	$6s^2$	97	Bk	$5f^97s^2$
20	Ca	$4s^2$	57	La	$5d^16s^2$	98	Cf	$5f^{10}7s^2$
21	Sc	$3d^14s^2$	58	Ce	$4f^15d^16s^2$	99	Es	$5f^{11}7s^2$
22	Ti	$3d^24s^2$	59	Pr	$4f^36s^2$	100	Fm	$5f^{12}7s^2$
23	V	$3d^34s^2$	60	Nd	$4f^46s^2$	101	Md	$5f^{13}7s^2$
24	Cr	$3d^44s^2$	61	Pm	$4f^56s^2$	102	No	$5f^{14}7s^2$
25	Mn	$3d^54s^2$	62	Sm	$4f^66s^2$	103	Lr	$5f^{14}6d^17s^2$
26	Fe	$3d^64s^2$	63	Eu	$4f^76s^2$	104	Rf	$5f^{14}6d^27s^2$
27	Co	$3d^74s^2$	64	Gd	$4f^75d^16s^2$	105	Db	$5f^{14}6d^37s^2$
28	Ni	$3d^84s^2$	65	Tb	$4f^96s^2$	106	Sg	$5f^{14}6d^47s^2$
29	Cu	$3d^94s^1$	66	Dy	$4f^{10}6s^2$	107	Bh	$5f^{14}6d^57s^2$
30	Zn	$3d^{10}4s^2$	67	Ho	$4f^{11}6s^2$	108	Hs	$5f^{14}6d^67s^2$
31	Ga	$3d^{10}4s^24p^1$	68	Er	$4f^{12}6s^2$	109	Mt	$5f^{14}6d^77s^2$
32	Ge	$3d^{10}4s^24p^2$	69	Tm	$4f^{13}6s^2$	110	Ds	$5f^{14}6d^87s^2$
33	As	$3d^{10}4s^24p^3$	70	Yb	$4f^{14}6s^2$	111	Rg	$5f^{14}6d^97s^2$
34	Se	$3d^{10}4s^24p^4$	71	Lu	$4f^{14}5d^16s^2$	112	Cn	$5f^{14}6d^{10}7s^2$
35	Br	$3d^{10}4s^24p^5$	72	Hf	$4f^{14}5d^26s^2$	113	Uut	$5f^{14}6d^{10}7s^27p^1$
36	Kr	$3d^{10}4s^24p^6$	73	Ta	$4f^{14}5d^36s^2$	114	Fl	$5f^{14}6d^{10}7s^27p^2$
			74	W	$4f^{14}5d^46s^2$	115	Uup	$5f^{14}6d^{10}7s^27p^3$
			75	Re	$4f^{14}5d^56s^2$	116	Lv	$5f^{14}6d^{10}7s^27p^4$
			76	Os	$4f^{14}5d^66s^2$	117	Uus	$5f^{14}6d^{10}7s^27p^5$
						118	Uuo	$5f^{14}6d^{10}7s^27p^6$

Fig. 3.22. Atomic electron configurations. The upper index shows the number of electrons in states with the indicated quantum numbers n (the first digit) and l (letter-coded as listed above).

The situation changes dramatically as we move to the next element, lithium (Li), with $Z = 3$ electrons. Two of them are still accommodated by the inner shell $n = 1$ (listed in Fig. 22 as the helium shell [He]), but the third one has to reside in the next shell with $n = 2$ and $l = 0$, i.e. in the $2s$ state. According to Eq. (191), the binding energy of this electron is much lower, especially if we take into account that according to Eq. (200), the $1s$ electrons of the [He] shell are much closer to the nucleus and almost completely compensate two thirds of its electric charge $+3e$. As a result, the $2s$ electron is reasonably well described by Eq. (199), with binding energy of just 5.39 eV, so that a lithium atom can give out that electron rather easily – to either atoms of other elements to form chemical compounds, or into the common conduction band of solid state lithium – and as a result it is a typical *alkali metal*. The similarity of chemical properties of lithium and hydrogen, with the *chemical valence* of one,⁷⁶ places Li as the starting element of the second *period* (row), with the first period limited to only H and He.

In the next element, beryllium ($Z = 4$), the $2s$ state ($n = 2$, $l = 0$) picks up one more electron, with the opposite spin. Due to the higher electric charge of the nucleus, $Q = 4e$, with only half of it compensated by $1s$ electrons of the [He] shell, the binding energy of the $2s$ electrons is higher than in lithium, so that the ionization energy increases to 9.32 eV. As a result, beryllium is also chemically active but not as active as lithium, with the valence of two, and is also metallic in its solid state phase, but does not conduct electric current as well as lithium.

Moving in this way along the second row of the periodic table (from $Z = 3$ to $Z = 10$), we see the gradual filling of all 4 different orbital states of the $n = 2$ shell, by 2 electrons each, with gradually growing ionization potential (up to 21.6 eV in Ne with $Z = 10$), i.e. the growing reluctance to have metallic conductance or form positive ions. However, the final elements of the row, such as oxygen (O, with $Z = 8$) and especially fluorine (F, with $Z = 9$) can readily pick up extra electrons to fill their $2p$ states, i.e. form negative ions. As a result, these elements are chemically active, with the double valence for oxygen and single valence for fluorine. However, the final element of this row, neon, has its $n = 2$ shell full, and cannot form a stable negative ion. This is why it is a noble gas, like helium. Traditionally, in the periodic table it is placed right under helium (Fig. 21), to emphasize the similarity of their chemical and physical properties. But this necessitates making an at least 6-cell gap in the 1st row. (Actually, the gap is often made larger, to accommodate next rows – keep reading.)

Period 3, i.e. the 3rd row of the table starts exactly like period 2, with sodium (Na, with $Z = 11$), also a chemically active alkali metal whose atom features 10 electrons filling shells with $n = 1$ and $n = 2$ (in Fig. 22 collectively called the neon shell, [Ne]), plus one electron in a $3s$ state ($n = 3$, $l = 0$, $m = 0$), which may be reasonably well described by the hydrogen atom theory – see, e.g., the red trace on the last panel of Fig. 20. Naively we could expect that, according to Eq. (194), and with the account of double spin degeneracy, this period of the table should have $2n^2 = 2 \times 3^2 = 18$ elements, with gradual filling of two $3s$ states, six $3p$ states, and ten $3d$ states. However, here we run into a big surprise: after argon (Ar, with $Z = 18$), a relatively inert element with ionization energy of 15.7 eV due to the fully filled $3s$ and $3p$ states, the next element, potassium (K, with $Z = 19$) is an alkali metal again!

The reason for that is the difference of the actual electron energies from those of the hydrogen atom, which is due mostly to inter-electron interactions and gradually accumulates with the growth of Z . It may be semi-quantitatively understood from the results of Sec. 6. In hydrogen-like atoms, electron state energies do not depend on the quantum number l (as well as m) – see Eq. (191). However, the

⁷⁶ Chemical valence is a relatively vague term describing the number of atom's electrons involved in chemical reactions. For the same atom, the number may depend on the chemical compound formed.

orbital quantum number does affect the wavefunction of an electron. As Fig. 20 shows, the larger l the less the probability for an electron to be close to the nucleus, where its positive charge is less compensated by other electrons. As a result of this effect (and also the relativistic corrections to be discussed in Sec. 6.3), electron's energy grows with l . Actually, this effect was visible even in period 2: it manifests itself in the filling order (p states after s states). However, for potassium (K, with $Z = 19$) and calcium (Ca, with $Z = 20$), energies of $3d$ states become so high that energies of two $4s$ states (with opposite spins) are lower, and they are filled first. As described by factor 3 in the square brackets of Eq. (200), and also by Eq. (201), the effect of the principal number n on the distance from the nucleus is stronger than that of $l < n$, so that $4s$ wavefunctions of K and Ca are relatively far from the nucleus, and determine the chemical valence (equal to 1 and 2, correspondingly) of these elements. The next atoms, from Sc ($Z = 21$) to Zn ($Z = 30$), with the gradually filled “internal” $3d$ states, are the so-called *transition metals* whose (comparable) ionization energies and chemical properties are determined by $4s$ electrons.

This fact is the origin of the difference between various forms of the “periodic” table. In its most popular option, shown in Fig. 21, K is used to start the next, period 4, and then a new period is started each time and only when the first electron with the next principal quantum number (n) appears.⁷⁷ This topology provides a very clear mapping on the chemical properties of the first element of each period (an alkali metal), as well as its last element (a noble gas). This also automatically means making gaps in all previous rows. Usually, this gap is made between the atoms with completely filled s states and with the first electron in a p state, because here the properties of the elements make a somewhat larger step. (For example, the step from Be to B makes the material an insulator, but it is not large enough to make a similar difference between Mg to Al.) As a result, elements of the same column have *approximately* similar chemical valence and physical properties.

However, to accommodate longer lowest rows, such presentation is inconvenient, because the whole table would be too broad. This is why the so-called *rare earths*, including *lanthanides* (with Z from 57 to 70, of the 6th row, with gradual filling of $4f$ and $5d$ states) and *actinides* (Z from 89 to 103, of the 7th row, with gradual filling of $5f$ and $6d$ states), are presented as outlet lines (Fig. 21). This is quite acceptable for the purposes of standard chemistry, because chemical properties of elements within each group are rather close.

To summarize, the “periodic table of elements” is not periodic in the strict sense of the word. Nevertheless, it has had an enormous historic significance for chemistry, as well as atomic and solid state physics, and is still very convenient for many purposes. For our course, the most important aspect of its discussion is the surprising possibility to describe, at least for classification purposes, such a complex multi-electron system as an atom as a set of quasi-independent electrons in certain quantum states indexed with the same quantum numbers n , l , and m as those of the hydrogen atom. This fact enables the use of various *perturbation theories*, which give more quantitative description of atomic properties. Some of these techniques will be reviewed in Chapters 6 and 8 of this course.⁷⁸

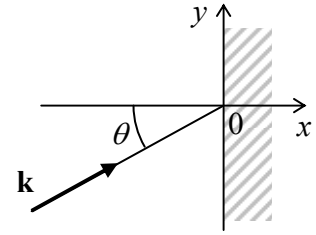
⁷⁷ Another option is to return to the first column as soon an atom has one electron in s state (like it is in Cu, Ag, and Au, in addition to the alkali metals).

⁷⁸ For a bit more detailed (but still very succinct) discussion of valence and other chemical aspects of atomic structure, I can recommend Chapter 5 of the classical text by L. Pauling, *General Chemistry*, Dover, 1988.

3.8. Exercise problems

3.1. A particle of energy E is incident (in Fig. on the right, within the plane of drawing) on a sharp potential step:

$$U(\mathbf{r}) = \begin{cases} 0, & \text{for } x < 0, \\ U_0, & \text{for } 0 < x. \end{cases}$$



Find the particle reflection probability R as a function of the incidence angle θ ; sketch and discuss the function, for different magnitudes and signs of U_0 .

3.2. Use the finite difference method with step $h = a/2$ to calculate as many eigenenergies as possible, for a free particle confined to the interior of:

- (i) a square with side a ;
- (ii) a cube with side a .

For the square, repeat the calculations, using a finer step: $h = a/3$. Compare the results for different h , with the exact formula.

Hint: It is advisable to first solve (or review the solution of :-) the similar 1D problem in Chapter 1, or start from reading about the finite difference method.⁷⁹ Also, try to exploit problem's symmetry.

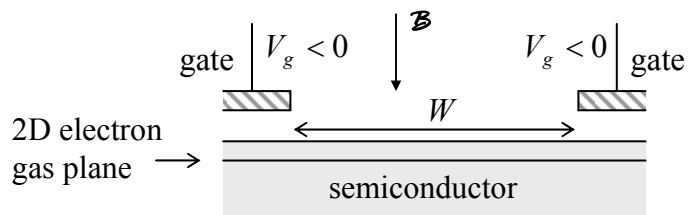
3.3. Use the variational method to estimate the ground state energy of a particle of mass m , moving in a spherically-symmetric potential

$$U(\mathbf{r}) = ar^4.$$

3.4. In the classical version of the Landau level problem discussed in Sec. 2, the center of particle's orbit is an integral of motion, determined by initial conditions. Calculate the commutation relations between the quantum-mechanical operators corresponding to the Cartesian coordinates of the center, and to the sum of their squares.

3.5.* Analyze how are the Landau levels (3.50) modified by an additional constant electric field $\mathbf{E}$, directed along the particle plane. Contemplate the physical meaning of your result, and its implications for the quantum Hall effect in a gate-defined Hall bar. (The area $L \times W$ area of such a bar [see Fig. 3.6 of the lecture notes] is defined by metallic gate electrodes parallel to the 2D electron gas plane - see Fig. on the right.

The negative voltage V_g , applied to the gates, chases the electrons gas out of the confinement plane at the remaining sample area.)



3.6. Analyze how are the Landau levels (50) modified if a 2D particle is confined in an additional 1D potential well $U(x) = m\omega_0^2 x^2/2$

⁷⁹ See, e.g., CM Sec. 8.5 or EM Sec. 2.8.

3.7. Find the eigenfunctions of a spinless, charged 3D particle moving in “crossed” (perpendicular), uniform electric and magnetic fields. For each eigenfunction, calculate the expectation value of particle’s velocity in the direction perpendicular to both fields, and compare the result with the solution of the corresponding classical problem.

Hint: Generalize Landau’s solution for 2D particles, discussed in Sec. 2.

3.8. Use the Born approximation to calculate the angular dependence and the full cross-section of scattering of an incident plane wave, propagating along axis x , by the following pair of point inhomogeneities:

$$U(\mathbf{r}) = W \left[\delta\left(\mathbf{r} - \mathbf{n}_z \frac{a}{2}\right) + \delta\left(\mathbf{r} + \mathbf{n}_z \frac{a}{2}\right) \right].$$

Analyze the results in detail. Derive the condition of the Born approximation’s validity for such delta-functional scatterers.

3.9. Use the Born approximation to calculate the differential and full cross-sections of a spherical scatterer:

$$U(\mathbf{r}) = \begin{cases} U_0, & \text{for } r < R, \\ 0, & \text{otherwise.} \end{cases}$$

Analyze both results, especially the angular dependence of $d\sigma/d\Omega$, in detail, for $kR \ll 1$ and $kR \gg 1$.

3.10. Use the Born approximation to calculate differential and full cross-sections of electron scattering by a screened Coulomb field of a point charge Ze , with electrostatic potential

$$\phi(\mathbf{r}) = \frac{Ze}{4\pi\epsilon_0 r} e^{-\lambda r},$$

neglecting the spin interaction effects, and analyzed their dependence on the screening parameter λ . Compare the results with those given by the classical (“Rutherford”) formula⁸⁰ for the unscreened Coulomb potential ($\lambda \rightarrow 0$), and formulate the condition of Born approximation’s validity in this limit.

3.11. A quantum particle of mass m with electric charge Q is scattered by a localized distributed charge with a spherically-symmetric density $\rho(r)$ and zero total charge. Use the Born approximation to calculate the differential cross-section of forward scattering (with scattering angle $\theta = 0$), and evaluate it for scattering of electrons by a hydrogen atom in its ground state.

3.12. Reformulate the Born approximation for the 1D case. Use the result to find the scattering and transfer matrices of a “rectangular” scatterer

$$U(x) = \begin{cases} U_0, & \text{for } |x| < d/2, \\ 0, & \text{otherwise.} \end{cases}$$

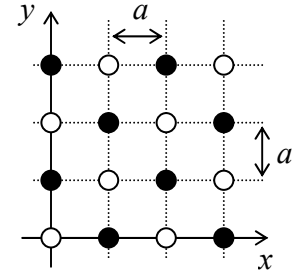
⁸⁰ See, e.g., CM Sec. 3.7, in particular Eq. (3.72).

Compare the results with the those of the exact calculations carried out earlier in the course.

3.13. Use Eq. (88) to show that the Bragg rule for the diffraction wave maxima, $\mathbf{k} = \mathbf{k}_0 + \mathbf{Q}$, where $\mathbf{Q}$ is any vector of the reciprocal lattice defined by Eq. (110), is valid not only for electromagnetic waves, but also for nonrelativistic quantum particle scattering by a periodic (Bravais) lattice.

3.14. In the tight-binding approximation, calculate the eigenstates and eigenvalues of three similar, weakly coupled quantum wells located in the vertices of an equilateral triangle.

3.15. Figure on the right shows a fragment of a periodic 2D lattice, with open and solid points showing the location of different local potentials – say, different atoms.



- (i) Find the reciprocal lattice and the 1st Brillouin zone;
- (ii) Find wave number k of the monochromatic radiation incident along axis x , at which the lattice creates the first-order diffraction peak within the $[x, y]$ plane, and the direction towards this peak.
- (iii) Semi-qualitatively, describe the evolution of the intensity of the peak if the local potentials represented by the open and solid points tend to each other.

3.16. For the 2D hexagonal lattice (Fig. 11b):

- (i) find the reciprocal lattice $\mathbf{Q}$ and the 1st Brillouin zone;
- (ii) use the tight-binding approximation to calculate the dispersion relation $E(\mathbf{q})$ for a 2D particle moving in a potential with such periodicity, close to the eigenenergy of an axially-symmetric state quasi-localized at the potential minima;
- (iii) analyze and sketch (or plot) the resulting dispersion relation $E(\mathbf{q})$ inside the 1st Brillouin zone.

3.17.* Complete the tight-binding approximation calculation of band structure of the honeycomb lattice, started in the end of Sec. 4. Analyze the results. Prove that the Dirac points $\mathbf{q}_D$ are located in the corners of the 1st Brillouin zone, and express the velocity v_n , participating in Eq. (122), in terms of the coupling energy δ_n . Show that the final results do not change if the quasi-localized wavefunctions are not axially-symmetric, but are proportional to $\exp\{in\varphi\}$ - as they are, with $n = 1$, for the $2p_z$ electrons of carbon atoms in graphene, which are responsible for its transport properties.

3.18. Examine basic properties of the so-called *Wannier functions* defined as

$$\phi_{\mathbf{R}}(\mathbf{r}) = \text{const} \times \int_{BZ} \psi_{\mathbf{q}}(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{R}} d^3q,$$

where $\psi_{\mathbf{q}}(\mathbf{r})$ is the Bloch wavefunction (3.108), $\mathbf{R}$ is any vector of the Bravais lattice, and the integration over quasi-momentum $\mathbf{q}$ is extended over any (e.g., the first) Brillouin zone.

3.19. Evaluate the long-range electrostatic interaction (the so-called *London dispersion force*) between two similar, electrically-neutral but polarizable molecules, modeling them as isotropic 3D harmonic oscillators.

Hint: Using the classical expression for the interaction between two electric dipoles,⁸¹ try to present the total Hamiltonian of the system as a sum of Hamiltonians of several independent harmonic oscillators, and calculate their ground-state energy as a function of distance between the molecules.

3.20. Use the variable separation method to find expressions for the eigenfunctions and the corresponding eigenenergies of a free 2D particle confined inside a thin round disk of radius R :

$$U = \begin{cases} 0, & \text{for } 0 \leq \rho < R, \\ +\infty, & \text{for } R < \rho, \end{cases}$$

where $\mathbf{p} \equiv \{x, y, 0\}$. What is the level degeneracy? Calculate 5 lowest energy levels with accuracy better than 1%.

3.21. Calculate the ground-state energy of a 2D particle localized in a shallow flat-bottom potential well

$$U(\rho) = \begin{cases} -U_0, & \text{for } \rho < R \\ 0, & \text{for } \rho > R \end{cases}, \quad \text{with } 0 < U_0 \ll \frac{\hbar^2}{mR^2}.$$

3.22. Spell out the explicit form of spherical harmonics $Y_4^0(\theta, \varphi)$ and $Y_4^4(\theta, \varphi)$.

3.23. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ in the ground state of the planar and spherical rotators of radius R . What can you say about averages $\langle p_x \rangle$ and $\langle p_x^2 \rangle$?

3.24. According to the discussion in the beginning of Sec. 5, eigenfunctions of a 3D harmonic oscillator may be calculated as products of three 1D “Cartesian oscillators” - see, in particular Eq. (124), with $d = 3$. However, according to the discussion in Sec. 3.6, wavefunctions of the type (190), proportional to spherical harmonics Y_l^m , are also eigenstates of this spherically-symmetric system. Represent:

- (i) the ground state of the oscillator, and
- (ii) each of its lowest excited states,

taken in the form (190), as linear combinations of products of 1D oscillator wavefunctions. Also, calculate the degeneracy of n^{th} energy level of the oscillator.

3.25. A spherical rotator (with $r \equiv (x^2 + y^2 + z^2)^{1/2} = R = \text{const}$) of mass m is in the state with wavefunction

$$\psi = \text{const} \times \left(\frac{1}{3} + \sin^2 \theta \right).$$

Calculate the system's energy.

3.26.* Calculate the eigenfunctions and the energy spectrum of a 3D particle free to move inside a sphere of radius R :

⁸¹ See, e.g., EM Sec. 3.1.

$$U = \begin{cases} 0, & \text{for } 0 \leq r < R, \\ +\infty, & \text{for } R < r. \end{cases}$$

Calculate 5 lowest energy levels with a 1% accuracy, and indicate the degeneracy of each level.

Hint: The solution of this problem requires the so-called *spherical Bessel functions* $j_l(\xi)$, whose description is available in most math handbooks.⁸²

3.27. Find the smallest value of depth U_0 for that the spherical quantum well

$$U = \begin{cases} -U_0, & \text{for } r < R, \\ 0, & \text{for } R < r, \end{cases}$$

has a bound (localized) eigenstate. Does such a state exist for a very narrow and deep well $U = -\mathcal{W}\delta(\mathbf{r})$, with a positive and finite $\mathcal{W}$?

3.28. Calculate the smallest value of depth U_0 for that the following spherically-symmetric quantum well,

$$U(r) = -U_0 e^{-r/R}, \quad \text{with } U_0, R > 0,$$

has a bound (localized) eigenstate.

Hint: Try to introduce the following new variables: $f \equiv rR$ and $\xi \equiv Ce^{-r/2R}$, with an appropriate choice of constant C .

3.29. Calculate the lifetime of the lowest metastable state in the spherical-shell potential

$$U(r) = \mathcal{W}\delta(r - R), \quad \text{with } \mathcal{W} > 0,$$

in the limit of large $\mathcal{W}$. Specify the limit of validity of your result.

3.30. Calculate the condition at which a particle of mass m , moving in the field of a very thin spherically-symmetric shell, with

$$U(\mathbf{r}) = -\mathcal{W}\delta(r - R), \quad \text{with } \mathcal{W} > 0,$$

has at least one localized (“bound”) stationary state. Compare the result with that for potential

$$U_0(\mathbf{r}) = -\mathcal{W}_0\delta(\mathbf{r}), \quad \text{with } \mathcal{W}_0 > 0.$$

Hint: Note that the first delta-function is one-dimensional, while the second one is three-dimensional, so that parameters $\mathcal{W}$ and $\mathcal{W}_0$ have different dimensionalities.

3.31. A particle, moving in a central potential $U(r)$, with $U(r) \rightarrow 0$ at $r \rightarrow \infty$, has a stationary state with the following wavefunction:

$$\psi = Cr^\alpha e^{-\beta r} \cos \theta,$$

where C , α , and β are constants. Calculate:

⁸² See, e.g., any of the handbooks recommended in MA Sec. 16(ii).

- (i) probabilities of all possible values of quantum numbers m and l ,
- (ii) the confining potential, and
- (iii) state's energy.

3.32. Calculate the energy spectrum of a particle moving in a monotonic, but otherwise arbitrary attractive central potential $U(r)$, in the approximation of large orbital quantum numbers l . Formulate the quantitative condition(s) of validity of your theory. Check that for the Coulomb potential $U(r) = -C/r$, your result agrees with Eq. (191).

3.33. An electron had been in the ground state of a hydrogen-like atom/ion with nuclear charge Ze , when the charge suddenly changed to $(Z + 1)e$.⁸³ Calculate the probabilities for the electron of the changed system to be:

- (i) in the ground state, and
- (ii) in the lowest excited state.

Evaluate these probabilities for the particular case of the beta decay of tritium, with the formation of a single-positive ion of ${}^3\text{He}$.

3.34. Calculate $\langle x^2 \rangle$ and $\langle p_x^2 \rangle$ in the ground state of a hydrogen-like atom. Compare the results with Heisenberg's uncertainty relation. What do these results tell about electron's velocity in the atom?

3.35. Apply to Eq. (181) the Hellmann-Feynman theorem (see Problem 1.4) to prove:

- (i) the first of Eqs. (3.201), and
- (ii) the fact that for a spinless particle in an arbitrary spherically-symmetric attractive potential $U(r)$, the ground state is always an s -state (with the orbital quantum number $l = 0$).

3.36. For the ground state of a hydrogen atom, calculate the expectation values of $\mathcal{E}$ and $\mathcal{E}^2$, where $\mathcal{E}$ is the electric field created by the atom at distance $r \gg r_0$ from its nucleus. Interpret the resulting relation between $\langle \mathcal{E} \rangle^2$ and $\langle \mathcal{E}^2 \rangle$ (at the same observation point).

⁸³ Such a fast change happens, for example, at the beta-decay, when one of nucleus' neutrons suddenly becomes a proton, emitting a high-energy electron and a neutrino which leave the system very fast (instantly on the atomic time scale), and do not participate in the atom transition's dynamics.

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Chapter 4. Bra-ket Formalism

The objective of this chapter is a discussion of Dirac's bra-ket formalism of quantum mechanics, which not only overcomes some inconveniences of wave mechanics, but also allows a natural description of such "internal" properties of particles as their spin. In the course of discussion of the formalism I will give several simple examples of its use, leaving more involved applications for the following chapters.

4.1. Motivation

We have seen that wave mechanics gives many results of primary importance. Moreover, it is fully (or mostly) sufficient for many applications, for example, for solid state electronics and device physics. However, in the course of our survey we have filed several grievances about this approach. Let me briefly summarize these complaints:

(i) Wave mechanics is focused on the *spatial* dependence of wavefunctions. On the other hand, our attempts to analyze the *temporal* evolution of quantum systems within this approach (beyond the trivial time behavior of the eigenfunctions, described by Eq. (1.61)), run into technical difficulties. For example, we could derive Eq. (2.159) describing time dynamics of the metastable state, or Eq. (2.185) describing quantum oscillations in coupled wells, only for the simplest potential profiles, though it is intuitively clear that these simple results should be common for all problem of this kind. Deriving the equations of such processes for arbitrary potential profiles is possible using perturbation theories (to be reviewed in Chapter 6), but that in the wave mechanics language they would require very bulky formulas.

(ii) The same is true concerning other issues that are conceptually addressable within wave mechanics, e.g., the Feynman path integral approach, description of coupling to environment, etc. Addressing them in wave mechanics would lead to formulas so bulky that I had (wisely :-) postponed them until we have got a more compact formalism on hand.

(iii) In the discussion of several key problems (for example the harmonic oscillator and spherically-symmetric potentials) we have run into rather complicated eigenfunctions coexisting with simple energy spectra - that infer some simple background physics. It is very important to get this physics revealed.

(iv) In the wave mechanics postulates, formulated in Sec. 1.2, quantum mechanical operators of the coordinate and momentum are treated very unequally – see Eqs. (1.26b). However, some key expressions, e.g., for the fundamental eigenfunction of a free-particle,

$$\exp\left\{i \frac{\mathbf{p} \cdot \mathbf{r}}{\hbar}\right\}, \quad (4.1)$$

or the harmonic oscillator's Hamiltonian,

$$\hat{H} = \frac{1}{2m} \hat{p}^2 + \frac{m\omega_0^2}{2} \hat{r}^2, \quad (4.2)$$

invite a similar treatment of momentum and coordinate.

However, the strongest motivation for a more general formalism comes from wave mechanics' conceptual incapability to describe elementary particles' *spins* and other internal quantum degrees of freedom, such as quark flavors or lepton numbers. In this context, let us review the basic facts on spin (which is a very representative and experimentally the most accessible of all internal quantum numbers), to understand what a more general formalism should explain - as a minimum.

Figure 1 shows the conceptual scheme of the simplest spin-revealing experiment, first carried out by O. Stern and W. Gerlach in 1922.¹ A collimated beam of electrons is passed through a gap between poles of a strong magnet, where the magnetic field $\mathcal{B}$, whose orientation is taken for axis z in Fig. 1, is non-uniform, so that both $\mathcal{B}_z$ and $d\mathcal{B}_z/dz$ are not equal to zero. As a result, the beam splits into two parts of equal intensity.

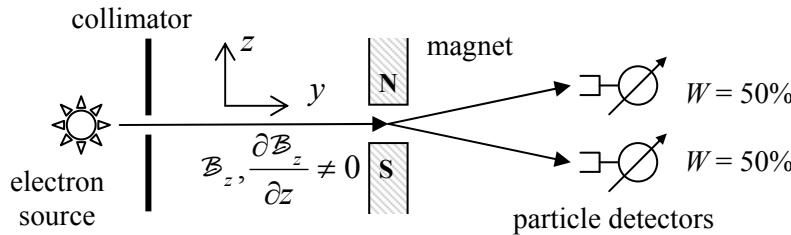


Fig. 4.1. The simplest Stern-Gerlach experiment.

This simplest experiment can be semi-quantitatively explained on classical, though somewhat phenomenological grounds by assuming that each electron has an intrinsic, permanent magnetic dipole moment $\mathbf{m}$. Indeed, classical electrodynamics² tells us that the potential energy U of a magnetic dipole in an external magnetic field is equal to $(-\mathbf{m} \cdot \mathcal{B})$, so that the force acting on the particle,

$$\mathbf{F} = -\nabla U = -\nabla(-\mathbf{m} \cdot \mathcal{B}), \quad (4.3)$$

has a nonvanishing vertical component

$$F_z = -\frac{\partial}{\partial z}(-m_z \cdot \mathcal{B}_z) = m_z \frac{\partial \mathcal{B}_z}{\partial z}. \quad (4.4)$$

Hence if we further postulate the existence of two possible, discrete values of $m_z = \pm\mu$, this explains the Stern-Gerlach effect qualitatively, as a result of the incident electrons having a random sign, but similar magnitude of m_z . A quantitative explanation of the beam splitting angle requires the magnitude of μ to be equal (or close) to the so-called *Bohr magneton*³

$$\mu_B \equiv \frac{\hbar e}{2m_e} \approx 0.9274 \times 10^{-23} \frac{\text{J}}{\text{T}}. \quad (4.5) \quad \text{Bohr magneton}$$

As we will see below, this value cannot be explained by any internal motion of the electron, say its rotation about axis z .

¹ To my knowledge, the concept of spin as an internal rotation of a particle was first suggested by R. Kronig, then a 20-year-old student, in January 1925, a few months before two other students, G. Uhlenbeck and S. Goudsmit - to whom the idea is usually attributed. The concept was then accepted and developed quantitatively by W. Pauli.

² See, e.g., EM Sec. 5.4, in particular Eq. (5.100).

³ A convenient mnemonic rule is that it is close to 1 K/T. In the Gaussian units, $\mu_B \equiv \hbar e / 2m_e c \approx 0.9274 \times 10^{-20}$.

Much more importantly, this semi-classical language cannot explain the results of the following set of multi-stage Stern-Gerlach experiments, shown in Fig. 2 - even qualitatively. In the first of the experiments, the electron beam is first passed through a magnetic field oriented (together with its gradient) along axis z , just as in Fig. 1. Then one of the two resulting beams is absorbed (or otherwise removed from the setup), while the other one is passed through a similar but x -oriented field. The experiment shows that this beam is split again into two components of equal intensity. A classical explanation of this experiment would require a very unnatural suggestion that the initial electrons had random but discrete components of the magnetic moment simultaneously in *two* directions, z and x .

However, even this assumption cannot explain the results of the three-stage Stern-Gerlach experiment shown on the middle panel of Fig. 2. Here, the previous two-state setup is complemented with one more absorber and one more magnet, now with the z -orientation again. Completely counter-intuitively, it again gives two beams of equal intensity, as if we have not yet filtered out the electrons with m_z corresponding to the lower beam, in the first, z -stage.

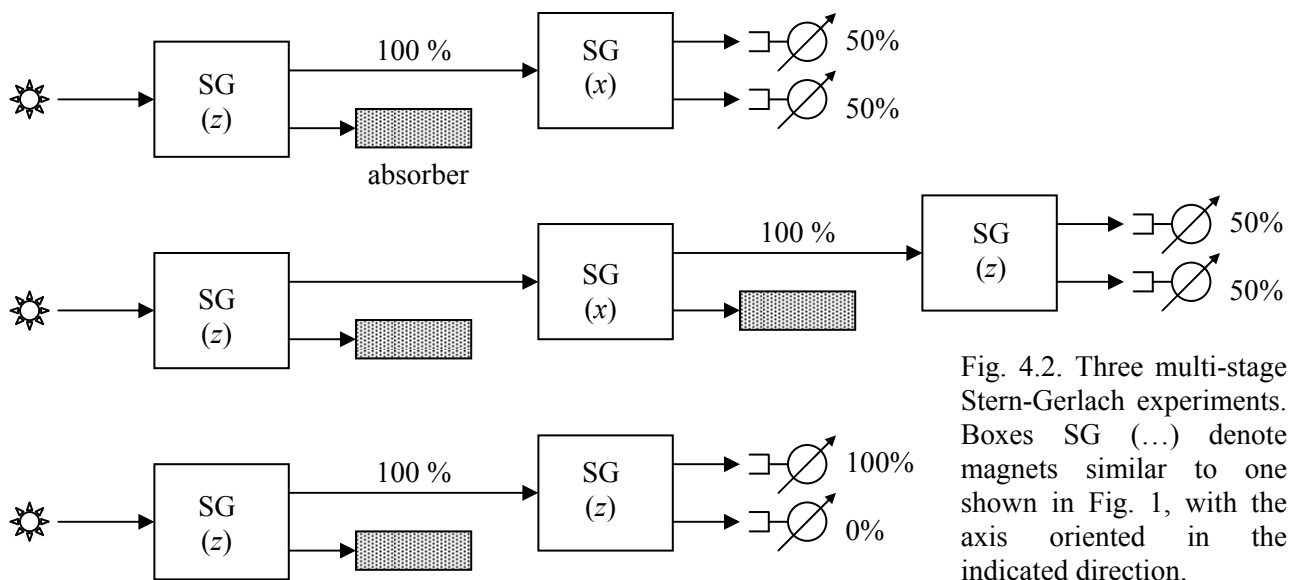


Fig. 4.2. Three multi-stage Stern-Gerlach experiments. Boxes SG (...) denote magnets similar to one shown in Fig. 1, with the axis oriented in the indicated direction.

The only way to save the classical explanation here is to say that maybe, electrons *somehow* interact with the magnetic field, so that the x -polarized (non-absorbed) beam becomes spontaneously depolarized again somewhere between magnetic stages. But any hope for such explanation is ruined by the control experiment shown on the bottom panel of Fig. 2, whose results indicate that no such depolarization happens.

We will see below that all these (and many more) results find a natural explanation in the *matrix mechanics* pioneered by W. Heisenberg, M. Born and P. Jordan in 1925. However, the matrix formalism is inconvenient for the solution of most problems discussed in Chapters 1-3, and for a time it was eclipsed by Schrödinger's wave mechanics, which had been put forward just a few months later. However, very soon P. A. M. Dirac introduced a more general *bra-ket formalism*, which provides a generalization of both approaches and proves their equivalence. Let me describe it.

4.2. States, state vectors, and linear operators

The basic notion of the general formulation of quantum mechanics is the *quantum state* of a system.⁴ To get some gut feeling of this notion, if a quantum state α of a particle may be adequately described by wave mechanics, this description is given by the corresponding wavefunction $\Psi_\alpha(\mathbf{r}, t)$. Note, however, the state as such is *not* a mathematical object (such as a function),⁵ and can participate in mathematical formulas only as a “pointer” – e.g., the index of function Ψ_α . On the other hand, the wavefunction is *not* a state, but a mathematical object (a complex function of space and time) giving a quantitative description of the state – just as the radius-vector as a function of time is a mathematical object describing the motion of a classical particle – see Fig. 3. Similarly, in the Dirac formalism a certain quantum state α is described by either of two mathematical objects, called the *state vectors*: the *ket-vector* $|\alpha\rangle$ and *bra-vector* $\langle\alpha|$.⁶

One should be cautious with the term “vector” here. Usual “geometric” vectors are defined in the usual geometric (say, Euclidean) space. In contrast, bra- and ket-vectors are defined in abstract *Hilbert spaces* of a given system,⁷ and, despite certain similarities with the geometric vectors, are new mathematical objects, so that we need new rules for handling them. The primary rules are essentially postulates and are justified only the correct description/prediction of all experimental observations their corollaries. While these is a general consensus among physicists what the corollaries are, there are many possible ways to carve from them the basic postulate sets. Just as in Sec. 1.2, I will not try too hard to beat the number of the postulates to the smallest possible minimum, trying instead to keep their physical meaning transparent.

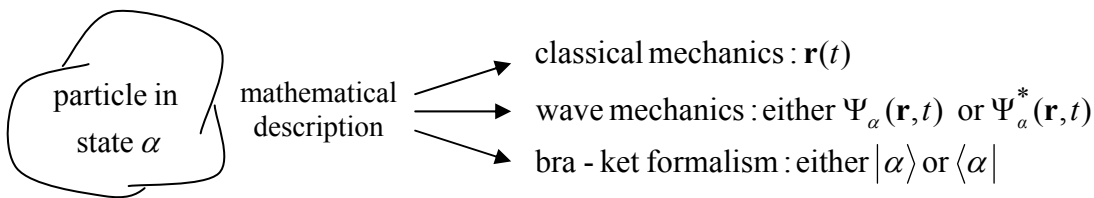


Fig. 4.3. Particle's state and its descriptions.

(i) Ket-vectors. Let us start with *ket-vectors* – sometimes called just *kets* for short. Perhaps the most important property of the vectors concerns their *linear superposition*. Namely, if several ket-vectors $|\alpha_j\rangle$ describe possible states of a quantum system, then any linear combination (*superposition*)

$$|\alpha\rangle = \sum_j c_j |\alpha_j\rangle, \quad (4.6)$$

Linear
superposition
of ket-vectors

⁴ An attentive reader could notice my smuggling term “system” instead of “particle” which was used in the previous chapters. Indeed, the bra-ket formalism allows the description of quantum systems much more complex than a single spinless particle that is a typical (though not the only possible) subject of wave mechanics.

⁵ As was expressed nicely by A. Peres, one of pioneers of the quantum information theory, “quantum phenomena do not occur in the Hilbert space, they occur in a laboratory”.

⁶ Terms *bra* and *ket* were suggested to reflect the fact that pair $\langle\beta|$ and $|\alpha\rangle$ may be considered as the set of parts of combination $\langle\beta|\alpha\rangle$ (see Eq. (11) below), which reminds an expression in the usual angle *brackets*.

⁷ The Hilbert space of a given system is defined as the set of all its possible state *vectors*. As should be clear from this definition, it is not advisable to speak about a “Hilbert space of quantum states”.

where c_j are any (possibly complex) c -numbers, also describes a possible state of the same system. (One may say that vector $|\alpha\rangle$ belongs to the same Hilbert space as all $|\alpha_j\rangle$.) Actually, since ket-vectors are new mathematical objects, the exact meaning of the right-hand part of Eq. (6) becomes clear only after we have postulated the following rules of summation of these vectors,

$$|\alpha_j\rangle + |\alpha_{j'}\rangle = |\alpha_{j'}\rangle + |\alpha_j\rangle, \quad (4.7)$$

and their multiplication by c -numbers:

$$c_j |\alpha_j\rangle = |\alpha_j\rangle c_j. \quad (4.8)$$

Note that in the set of wave mechanics postulates, statements parallel to (7) and (8) were unnecessary, because wavefunctions are the usual (albeit complex) functions of space and time, and we know from the usual algebra that such relations are valid.

As evident from Eq. (6), the complex coefficient c_j may be interpreted as the “weight” of state α_j in the linear superposition α . One important particular case is $c_j = 0$, showing that state α_j does not participate in the superposition α . By the way, the corresponding term of sum (6), i.e. product

Null-state
vector

$$0|\alpha_j\rangle, \quad (4.9)$$

has a special name: the *null-state* vector. (It is important to avoid confusion between the null-state corresponding to vector (9), and the ground state of the system, which is frequently denoted by ket-vector $|0\rangle$. In some sense, the null-state does not exist at all, while the ground state does – and frequently is the most important quantum state of the system.)

(ii) Bra-vectors and inner (“scalar”) products. Bra-vectors $\langle\alpha|$, which obey the rules similar to Eqs. (7) and (8), are not new, independent objects: if a ket-vector $|\alpha\rangle$ is known, the corresponding bra-vector $\langle\alpha|$ describes the same state. In other words, there is a *unique dual correspondence* between $|\alpha\rangle$ and $\langle\alpha|$,⁸ very similar (though not identical) to that between a wavefunction Ψ and its complex conjugate Ψ^* . The correspondence between these vectors is described by the following rule: if a ket-vector of a linear superposition is described by Eq. (6), then the corresponding bra-vector is

Linear
superposition
of bra-vectors

$$\langle\alpha| = \sum_j c_j^* \langle\alpha_j| = \sum_j \langle\alpha_j| c_j^*. \quad (4.10)$$

The mathematical convenience of using two types of vectors, rather than just one, becomes clear from the notion of their *inner product* (also called the *short bracket*):

Inner
bra-ket
product

$$\langle\beta|\alpha\rangle \equiv \langle\beta|\alpha\rangle. \quad (4.11)$$

This is a (generally, complex)⁹ *scalar*, whose main property is the linearity with respect to any of its component vectors. For example, if a linear superposition α is described by the ket-vector (6), then

⁸ Mathematicians like to say that the ket- and bra-vectors of the same quantum system are defined in two *isomorphic Hilbert spaces*.

⁹ This is one of the differences of bra- and ket-vectors from the usual (geometrical) vectors whose scalar product is always a real scalar.

$$\langle \beta | \alpha \rangle = \sum_j c_j \langle \beta | \alpha_j \rangle, \quad (4.12)$$

while if Eq. (10) is true, then

$$\langle \alpha | \beta \rangle = \sum_j c_j^* \langle \alpha_j | \beta \rangle. \quad (4.13)$$

In plain English, c -numbers may be moved either into, or out of the inner products.

The second key property of the inner product is

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle^*. \quad (4.14)$$

Inner
product's
complex
conjugate

It is compatible with Eq. (10); indeed, the complex conjugation of both parts of Eq. (12) gives:

$$\langle \beta | \alpha \rangle^* = \sum_j c_j^* \langle \beta | \alpha_j \rangle^* = \sum_j c_j^* \langle \alpha_j | \beta \rangle = \langle \alpha | \beta \rangle. \quad (4.15)$$

Finally, one more rule: the inner product of the bra- and ket-vectors describing the same state (called the *norm squared*) is real and non-negative,

$$\|\alpha\|^2 \equiv \langle \alpha | \alpha \rangle \geq 0. \quad (4.16)$$

State's
norm
squared

In order to give the reader some feeling about the meaning of this rule: we will show below that if state α may be described by wavefunction $\Psi_\alpha(\mathbf{r}, t)$, then

$$\langle \alpha | \alpha \rangle = \int \Psi_\alpha^* \Psi_\alpha d^3r \geq 0. \quad (4.17)$$

Hence the role of the bra-ket is very similar to the complex conjugation of the wavefunction, and Eq. (10) emphasizes this similarity. (Note that, by convention, there is no conjugation sign in the bra-part of the inner product; its role is played by the angular bracket inversion.)

(iii) Operators. One more key notion of the Dirac formalism are quantum-mechanical *linear operators*. Just as for the operators discussed in wave mechanics, the function of an operator is the “generation” of one state from another: if $|\alpha\rangle$ is a possible ket of the system, and $\hat{A}$ is a legitimate operator, then the following combination,

$$\hat{A}|\alpha\rangle, \quad (4.18)$$

is also a ket-vector describing a possible state of the system, i.e. a ket-vector in the same Hilbert space as the initial vector $|\alpha\rangle$. As follows from the adjective “linear”, the main rules governing the operators is their linearity with respect to both any superposition of vectors:

$$\hat{A}\left(\sum_j c_j |\alpha_j\rangle\right) = \sum_j c_j \hat{A}|\alpha_j\rangle, \quad (4.19)$$

and any superposition of operators:

$$\left(\sum_j c_j \hat{A}_j\right)|\alpha\rangle = \sum_j c_j \hat{A}_j|\alpha\rangle. \quad (4.20)$$

These rules are evidently similar to Eqs. (1.53)-(1.54) of wave mechanics.

The above rules imply that an operator “acts” on the ket-vector on its right; however, a combination of the type $\langle\alpha|\hat{A}$ is also legitimate and presents a new bra-vector. It is important that, generally, this vector does *not* represent the same state as ket-vector (18); instead, the bra-vector isomorphic to ket-vector (18) is

$$\langle\alpha|\hat{A}^\dagger. \quad (4.21)$$

This statement serves as the definition of the *Hermitian conjugate* (or “Hermitian adjoint”) $\hat{A}^\dagger$ of the initial operator $\hat{A}$. For an important class of operators, called the *Hermitian operators*, the conjugation is inconsequential, i.e. for them

$$\hat{A}^\dagger = \hat{A}. \quad (4.22)$$

(This equality, as well as any other operator equation below, means that these operators act similarly on any bra- or ket-vector.)¹⁰

To proceed further, we need an additional postulate, called the *associative axiom of multiplication*: into *any* legitimate bra-ket expression,¹¹ not including an explicit summation, we may insert or remove parentheses (just in the ordinary product of scalars), meaning as usual that the operation inside the parentheses is performed first. The first two examples of this postulate are given by Eqs. (19) and (20), but the associative axiom is more general and says, for example:

$$\langle\beta|(\hat{A}|\alpha\rangle) = (\langle\beta|\hat{A})|\alpha\rangle \equiv \langle\beta|\hat{A}|\alpha\rangle, \quad (4.23)$$

This equality serves as the definition of the last form, called the *long bracket* (evidently, also a scalar), with an operator sandwiched between a bra-vector and a ket-vector. This definition, when combined with the definition of the Hermitian conjugate and Eq. (14), yields an important corollary:

$$\langle\beta|\hat{A}|\alpha\rangle = \langle\beta|(\hat{A}|\alpha\rangle) = \left(\left(\langle\alpha|\hat{A}^\dagger \right) |\beta\rangle \right)^* = \langle\alpha|\hat{A}^\dagger|\beta\rangle^*, \quad (4.24)$$

which is most frequently rewritten as

$$\langle\alpha|\hat{A}|\beta\rangle^* = \langle\beta|\hat{A}^\dagger|\alpha\rangle. \quad (4.25)$$

The associative axiom also enables to readily explore the following definition of one more, *outer* product of bra- and ket-vectors:

¹⁰ If we consider *c*-numbers as a particular type of operators, then according to Eqs. (11) and (21), for them the Hermitian conjugation is equivalent to the simple complex conjugation, so that only a real *c*-number may be considered as a particular case of the Hermitian operator (22).

¹¹ Here “legitimate” means “having a clear sense in the bra-ket formalism”. Some examples of “illegitimate” expressions: $|\alpha\rangle\hat{A}$, $\hat{A}\langle\alpha|$, $|\alpha\rangle|\beta\rangle$, $\langle\alpha|\langle\beta|$. Note, however, that the last two expressions may be legitimate if α and β are states of different systems, i.e. if their state vectors belong to different Hilbert spaces. We will run into such *tensor products* of bra- and ket vectors (sometimes denoted, respectively, as $|\alpha\rangle\otimes|\beta\rangle$ and $\langle\alpha|\otimes\langle\beta|$) in Chapters 6-8.

$$|\beta\rangle\langle\alpha|. \quad (4.26)$$

Outer
bra-ket
product

In contrast to the inner product (12), which is a *scalar*, this mathematical construct is an *operator*. Indeed, the associative axiom allows us to remove parentheses in the following expression:

$$(|\beta\rangle\langle\alpha|)|\gamma\rangle = |\beta\rangle\langle\alpha|\gamma\rangle. \quad (4.27)$$

But the last bra-ket is just a scalar; hence the mathematical object (26) acting on a ket-vector (in this case, $|\gamma\rangle$) gives a new ket-vector, which is the essence of operator's action. Very similarly,

$$\langle\delta|(|\beta\rangle\langle\alpha|) = \langle\delta|\beta\rangle\langle\alpha| \quad (4.28)$$

- again a typical operator's action on a bra-vector.

Now let us perform the following calculation. We may use the parentheses insertion into the bra-ket equality following from Eq. (14),

$$\langle\gamma|\alpha\rangle\langle\beta|\delta\rangle = (\langle\delta|\beta\rangle\langle\alpha|\gamma\rangle)^*, \quad (4.29)$$

to transform it to the following form:

$$\langle\gamma|(|\alpha\rangle\langle\beta|)|\delta\rangle = (\langle\delta|(|\beta\rangle\langle\alpha|)|\gamma\rangle)^*. \quad (4.30)$$

Since this equation should be valid for any vectors $\langle\gamma|$ and $|\beta\rangle$, its comparison with Eq. (25) gives the following operator equality

$$(|\alpha\rangle\langle\beta|)^\dagger = |\beta\rangle\langle\alpha|. \quad (4.31)$$

Outer
product's
Hermitian
conjugate

This is the conjugate rule for outer products; it reminds rule (14) for inner products, but involves the Hermitian (rather than the usual complex) conjugation.

The associative axiom is also valid for the operator “multiplication”:

$$(\hat{A}\hat{B})|\alpha\rangle = \hat{A}(\hat{B}|\alpha\rangle), \quad \langle\beta|(\hat{A}\hat{B}) = (\langle\beta|\hat{A})\hat{B}, \quad (4.32)$$

showing that the action of an operator product on a state vector is nothing more than the sequential action of the operands. However, we have to be rather careful with the operator products; generally they do not commute: $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. This is why the *commutator*, the operator defined as

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}, \quad (4.33)$$

Commutator

is a very useful option. Another similar notion is the *anticommutator*:¹²

$$\{\hat{A}, \hat{B}\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}. \quad (4.34)$$

Anti-
commutator

Finally, the bra-ket formalism broadly uses two special operators: the *null operator* $\hat{0}$ defined by the following relations:

¹² Another popular notation for the anticommutator is $[\hat{A}, \hat{B}]_+$; it will not be used in these notes.

Null
operator

$$\hat{0}|\alpha\rangle \equiv 0|\alpha\rangle, \quad \langle\alpha|\hat{0} \equiv \langle\alpha|0, \quad (4.35)$$

for an arbitrary state α , we may say that the null operator “kills” *any* state, turning it into the null-state. Another elementary operator is the *identity operator*, which is also defined by its action (or rather “inaction” :-)) on an arbitrary state vector:

Identity
operator

$$\hat{I}|\alpha\rangle \equiv |\alpha\rangle, \quad \langle\alpha|\hat{I} \equiv \langle\alpha|. \quad (4.36)$$

4.3. State basis and matrix representation

While some operations in quantum mechanics may be carried out in the general bra-ket formalism outlined above, most calculations are done for specific quantum systems that feature at least one *full and orthonormal* set $\{u\}$ of states u_j , frequently called a *basis*. These terms mean that any state vector of the system may be represented as a unique sum of the type (6) or (10) over its basis vectors:

Expansion
over
basis
vectors

$$|\alpha\rangle = \sum_j \alpha_j |u_j\rangle, \quad \langle\alpha| = \sum_j \alpha_j^* \langle u_j|, \quad (4.37)$$

(so that, in particular, if α is one of the basis states, say $u_{j'}$, then $\alpha_j = \delta_{jj'}$), and that

Basis
vectors'
ortho-
normality

$$\langle u_j | u_{j'} \rangle = \delta_{jj'}. \quad (4.38)$$

For the systems that may be described by wave mechanics, examples of the full orthonormal bases are represented by any orthonormal set of eigenfunctions calculated in the previous 3 chapters – as the simplest example, see Eq. (1.76).

Due to the uniqueness of expansion (37), the full set of coefficients α_j gives a complete description of state α (in a fixed basis $\{u\}$), just as the usual Cartesian components A_x , A_y , and A_z give a complete description of a usual geometric 3D vector $\mathbf{A}$ (in a fixed reference frame). Still, let me emphasize some differences between the quantum-mechanical bra- and ket-vectors and the usual geometric vectors:

- (i) a basis set may have a large or even infinite number of states u_j , and
- (ii) the expansion coefficients α_j may be complex.

With these reservations in mind, the analogy with geometric vectors may be pushed even further. Let us inner-multiply both parts of the first of Eqs. (37) by a bra-vector $\langle u_{j'}|$ and then transform the relation using the linearity rules discussed in the previous section, and Eq. (38):

$$\langle u_{j'} | \alpha \rangle = \langle u_{j'} | \sum_j \alpha_j |u_j\rangle = \sum_j \alpha_j \langle u_{j'} | u_j \rangle = \alpha_{j'}, \quad (4.39)$$

Together with Eq. (14), this means that any of the expansion coefficients in Eq. (37) may be presented as an inner product:

Expansion
coefficients
as inner
products

$$\alpha_j = \langle u_j | \alpha \rangle, \quad \alpha_j^* = \langle \alpha | u_j \rangle; \quad (4.40)$$

these relations are analogs of equalities $A_j = \mathbf{n}_j \cdot \mathbf{A}$ of the usual vector algebra. Using these important relations (which we will use on numerous occasions), expansions (37) may be rewritten as

$$|\alpha\rangle = \sum_j |u_j\rangle \langle u_j | \alpha \rangle \equiv \sum_j \hat{\Lambda}_j |\alpha\rangle, \quad \langle \alpha | = \sum_j \langle \alpha | u_j \rangle \langle u_j | \equiv \sum_j \langle \alpha | \hat{\Lambda}_j, \quad (4.41)$$

A comparison of these relations with Eq. (26) shows that the outer product defined as

$$\hat{\Lambda}_j \equiv |u_j\rangle \langle u_j|, \quad (4.42)$$

Projection
operator

is a legitimate linear operator. Such an operator, acting on any state vector of the type (37), singles out just one of its components, for example,

$$\hat{\Lambda}_j |\alpha\rangle = |u_j\rangle \langle u_j | \alpha \rangle = \alpha_j |u_j\rangle, \quad (4.43)$$

i.e. kills all components of the linear superposition but one. In the geometric analogy, such operator “projects” the state vector on its (j^{th}) “direction”, hence its name – the *projection operator*. Probably, the most important property of the projection operators, called the *closure* (or *completeness*) *relation*, immediately follows from Eq. (41): their sum over the full basis is equivalent to the identity operator:

$$\sum_j |u_j\rangle \langle u_j| = \hat{I}. \quad (4.44)$$

Closure
relation

This means in particular that we may insert the left-hand part of Eq. (44) into any bra-ket relation, at any place – the trick that we will use again and again.

Let us see how expansions (37) transform all the notions introduced in the last section, starting from the short bra-ket (11) (the inner product of two state vectors):

$$\langle \beta | \alpha \rangle = \sum_{j,j'} \langle u_j | \beta_j^* \alpha_{j'} | u_{j'} \rangle = \sum_{j,j'} \beta_j^* \alpha_{j'} \delta_{jj'} = \sum_j \beta_j^* \alpha_j. \quad (4.45)$$

Besides the complex conjugation, this expression is similar to the scalar product of the usual vectors. Now, let us explore the long bra-ket (23):

$$\langle \beta | \hat{A} | \alpha \rangle = \sum_{j,j'} \beta_j^* \langle u_j | \hat{A} | u_{j'} \rangle \alpha_{j'} \equiv \sum_{j,j'} \beta_j^* A_{jj'} \alpha_{j'}. \quad (4.46)$$

Here, the last step uses a very important notion of *matrix elements* of the operator, defined as

$$A_{jj'} \equiv \langle u_j | \hat{A} | u_{j'} \rangle. \quad (4.47)$$

Operator's
matrix
elements

As evident from Eq. (46), the full set of the matrix elements completely characterizes the operator, just as the full set of expansion coefficients (40) fully characterizes a quantum state. The term “matrix” means, first of all, that it is convenient to present the full set of $A_{jj'}$ as a square table (*matrix*), with the linear dimension equal to the number of basis states u_j of the system under the consideration, i.e. the size of its Hilbert space.

As two simplest examples, all matrix elements of the null-operator, defined by Eqs. (35), are evidently equal to zero (in any basis), and hence it may be presented as a matrix of zeros (the *null matrix*):

$$0 \equiv \begin{pmatrix} 0 & 0 & \dots \\ 0 & 0 & \dots \\ \dots & \dots & \dots \end{pmatrix}, \quad (4.48)$$

Null
matrix

while for the identity operator $\hat{I}$, defined by Eqs. (36), we readily get

$$I_{jj'} = \langle u_j | \hat{I} | u_{j'} \rangle = \langle u_j | u_{j'} \rangle = \delta_{jj'}, \quad (4.49)$$

i.e. its matrix (called the *identity matrix*) is diagonal – also in any basis:

Identity
matrix

$$I \equiv \begin{pmatrix} 1 & 0 & \dots \\ 0 & 1 & \dots \\ \dots & \dots & \dots \end{pmatrix}. \quad (4.50)$$

The convenience of the matrix language extends well beyond the presentation of particular operators. For example, let us use definition (47) to calculate matrix elements for a product of two operators:

$$(AB)_{jj''} = \langle u_j | \hat{A}\hat{B} | u_{j''} \rangle. \quad (4.51)$$

Here we can use Eq. (44) for the first (but not the last!) time, inserting the identity operator between the two operators, and then expressing it via a sum of projection operators:

Matrix
element
of an
operator
product

$$(AB)_{jj''} = \langle u_j | \hat{A}\hat{B} | u_{j''} \rangle = \langle u_j | \hat{A}\hat{I}\hat{B} | u_{j''} \rangle = \sum_{j'} \langle u_j | \hat{A} | u_{j'} \rangle \langle u_{j'} | \hat{B} | u_{j''} \rangle = \sum_{j'} A_{jj'} B_{j'j''}. \quad (4.52)$$

This result corresponds to the standard “row by column” rule of calculation of an arbitrary element of the matrix product

$$AB = \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} & \dots \\ B_{21} & B_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix}. \quad (4.53)$$

Hence the product of operators may be presented (in a fixed basis!) by that of their matrices (in the same basis). This is so convenient that the same language is often used to present not only the long bracket,

Long
bracket
as a matrix
product

$$\langle \beta | \hat{A} | \alpha \rangle = \sum_{j'} \beta_j^* A_{jj'} \alpha_{j'} = \begin{pmatrix} \beta_1^* & \beta_2^* & \dots \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \dots \end{pmatrix}, \quad (4.54)$$

but even the simpler short bracket:

Short
bracket
as a matrix
product

$$\langle \beta | \alpha \rangle = \sum_j \beta_j^* \alpha_j = \begin{pmatrix} \beta_1^* & \beta_2^* & \dots \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \dots \end{pmatrix}, \quad (4.55)$$

although these equalities require the use of non-square matrices: rows of (complex-conjugate!) expansion coefficients for the presentation of bra-vectors, and columns of these coefficients for the presentation of ket-vectors. With that, the mapping of states and operators on matrices becomes completely general.

Now let us have a look at the outer product operator (26). Its matrix elements are just

$$(|\alpha\rangle\langle\beta|)_{jj'} = \langle u_j | \alpha \rangle \langle \beta | u_{j'} \rangle = \alpha_j \beta_{j'}^*. \quad (4.56)$$

These are elements of a very special square matrix, whose filling requires the knowledge of just $2N$ scalars (where N is the basis set size), rather than N^2 scalars as for an arbitrary operator. However, a simple generalization of such outer product may present an arbitrary operator. Indeed, let us insert two identity operators (44), with different summation indices, on both sides of any operator:

$$\hat{A} = \hat{I}\hat{A}\hat{I} = \left(\sum_j |u_j\rangle\langle u_j| \right) \hat{A} \left(\sum_{j'} |u_{j'}\rangle\langle u_{j'}| \right), \quad (4.57)$$

and use the associative axiom to rewrite this expression as

$$\hat{A} = \sum_{j,j'} |u_j\rangle\langle u_j| \hat{A} |u_{j'}\rangle\langle u_{j'}|. \quad (4.58)$$

But the expression in the middle long bracket is just the matrix element (47), so that we may write

$$\hat{A} = \sum_{j,j'} |u_j\rangle A_{jj'} \langle u_{j'}|. \quad (4.59)$$

Operator's
expression
via its
matrix
elements

The reader has to agree that this formula, which is a natural generalization of Eq. (44), is extremely elegant. Also note the following parallel: if we consider the matrix element definition (47) as some sort of analog of Eq. (40), then Eq. (59) is a similar analog of the expansion expressed by Eq. (37).

The matrix presentation is so convenient that it makes sense to move it by one level lower – from state vector products to “bare” state vectors resulting from operator’s action upon a given state. For example, let us use Eq. (59) to present the ket-vector (18) as

$$|\alpha'\rangle \equiv \hat{A}|\alpha\rangle = \left(\sum_{j,j'} |u_j\rangle A_{jj'} \langle u_{j'}| \right) |\alpha\rangle = \sum_{j,j'} |u_j\rangle A_{jj'} \langle u_{j'} | \alpha \rangle. \quad (4.60)$$

According to Eq. (40), the last short bracket is just $\alpha_{j'}$, so that

$$|\alpha'\rangle = \sum_{j,j'} |u_j\rangle A_{jj'} \alpha_{j'} = \sum_j \left(\sum_{j'} A_{jj'} \alpha_{j'} \right) |u_j\rangle \quad (4.61)$$

But expression in middle parentheses is just the coefficient α'_j of expansion (37) of the resulting ket-vector (60) in the same basis, so that

$$\alpha'_j = \sum_{j'} A_{jj'} \alpha_{j'}. \quad (4.62)$$

This result corresponds to the usual rule of multiplication of a matrix by a column, so that we may represent any ket-vector by its column matrix, with the operator action looking like

$$\begin{pmatrix} \alpha'_1 \\ \alpha'_2 \\ \dots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \dots \end{pmatrix}. \quad (4.63)$$

Absolutely similarly, the operator action on the bra-vector (21), represented by its row-matrix, is

$$(\alpha_1'^*, \alpha_2'^*, \dots) = (\alpha_1^*, \alpha_2^*, \dots) \begin{pmatrix} \left(A^\dagger \right)_{11} & \left(A^\dagger \right)_{12} & \dots \\ \left(A^\dagger \right)_{21} & \left(A^\dagger \right)_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix}. \quad (4.64)$$

By the way, Eq. (64) naturally raises the following question: what are the elements of the matrix in its right-hand part, or more exactly, what is the relation between the matrix elements of an operator and its Hermitian conjugate? The simplest way to get an answer is to use Eq. (25) with two arbitrary states (say, u_j and $u_{j'}$) of the same basis in the role of α and β . Together with the orthonormality relation (38), this immediately gives¹³

Hermitian
conjugate's
matrix
elements

$$\left(\hat{A}^\dagger \right)_{jj'} = \left(A_{j'j} \right)^*. \quad (4.65)$$

Thus, the matrix of the Hermitian conjugate operator is the *complex conjugated and transposed* matrix of the initial operator. This result exposes very clearly the essence of the Hermitian conjugation. It also shows that for the Hermitian operators, defined by Eq. (22),

$$A_{jj'} = A_{j'j}^*, \quad (4.66)$$

i.e. any pair of their matrix elements, symmetric about the main diagonal, should be complex conjugate of each other. As a corollary, the main-diagonal elements have to be real:

$$A_{jj} = A_{jj}^*, \quad \text{i.e. } \text{Im } A_{jj} = 0. \quad (4.67)$$

(Matrix (50) evidently satisfies Eq. (66), so that the identity operator is Hermitian.)

In order to fully appreciate the special role played by Hermitian operators in the quantum theory, let us introduce the key notions of *eigenstates* a_j (described by their *eigenvectors* $\langle a_j |$ and $| a_j \rangle$) and *eigenvalues* (c-numbers) A_j of an operator $\hat{A}$, defined by the equation they have to satisfy:¹⁴

Operator's
eigenstates
and
eigenvalues

$$\hat{A} | a_j \rangle = A_j | a_j \rangle. \quad (4.68)$$

Let us prove that eigenvalues of any Hermitian operator are real,¹⁵

Hermitian
operator's
eigenvalues

$$A_j = A_j^*, \quad \text{for } j = 1, 2, \dots, N, \quad (4.69)$$

¹³ For the sake of formula compactness, below I will use the shorthand notation in which the operands of this equality are just $A_{jj'}^\dagger$ and $A_{j'j}^*$. I believe that it leaves little chance for confusion, because the Hermitian conjugation sign $\dagger$ may pertain only to an operator (or its matrix), while the complex conjugation sign $*$ to a scalar – say a matrix element.

¹⁴ This equation should look familiar to the reader – see the stationary Schrödinger equation (1.60), which was the focus of our studies in the first three chapters. We will see soon that that equation is just a particular (coordinate) representation of Eq. (66) for the Hamiltonian as the operator of energy.

¹⁵ The reciprocal statement is also true: if all eigenvalues of an operator are real, it is Hermitian (in any basis). This statement may be readily proved by applying Eq. (93) below to the case when $A_{kk'} = A_k \delta_{kk'}$, with $A_k^* = A_k$.

while the eigenstates corresponding to different eigenvalues are orthogonal:

$$\langle a_j | a_{j'} \rangle = 0, \quad \text{if } A_j \neq A_{j'}. \quad (4.70)$$

Hermitian
operator's
eigenvectors

The proof of both statements is surprisingly simple. Let us inner-multiply both sides of Eq. (68) by bra-vector $\langle a_{j'} |$. In the right-hand part of the result, the eigenvalue A_j , as a c -number, may be taken out of the bra-ket, giving

$$\langle a_{j'} | \hat{A} | a_j \rangle = A_j \langle a_{j'} | a_j \rangle. \quad (4.71)$$

This equality should hold for any pair of eigenstates, so that we may swap the indices in Eq. (71), and complex-conjugate the result:

$$\langle a_j | \hat{A} | a_{j'} \rangle^* = A_{j'}^* \langle a_j | a_{j'} \rangle^*. \quad (4.72)$$

Now using Eqs. (14) and (25), together with the Hermitian operator definition (22), we may transform Eq. (72) to the following form:

$$\langle a_{j'} | \hat{A} | a_j \rangle = A_{j'}^* \langle a_{j'} | a_j \rangle. \quad (4.73)$$

Subtracting this equation from Eq. (71), we get

$$0 = (A_j - A_{j'}^*) \langle a_{j'} | a_j \rangle. \quad (4.74)$$

There are two possibilities to satisfy this equation. If indices j and j' are equal (denote the same eigenstate), then the bra-ket is the state's norm squared, and cannot be equal to zero. Then the left parentheses (with $j = j'$) have to be zero, i.e. Eq. (69) is valid. On the other hand, if j and j' correspond to different eigenstates, the parentheses cannot equal zero (we have just proved that all A_j are real!), and hence the state vectors indexed by j and j' should be orthogonal, e.g., Eq. (70) is valid.

As will be discussed below, these properties make Hermitian operators suitable for the description of physical observables.

4.4. Change of basis and matrix diagonalization

From the discussion of last section, it may look that the matrix language is fully similar to, and in many instances more convenient than the general bra-ket formalism. In particular, Eqs. (52), (54), (55) show that any part of any bra-ket expression may be directly mapped on the similar matrix expression, with the only slight inconvenience of using not only columns, but also rows (with their elements complex-conjugated), for state vector presentation. In this context, why do we need the bra-ket language at all? The answer is that the elements of the matrices depend on the particular choice of the basis set, very much like the Cartesian components of a usual vector depend on the particular choice of reference frame orientation (Fig. 4), and very frequently it is convenient to use two or more different basis sets for the same system.

With this motivation, let us study what happens if we change from one basis, $\{u\}$, to another one, $\{v\}$ - both full and orthonormal. First of all, let us prove that for each such pair of bases, there exists such an operator $\hat{U}$ that, first,

Basis
transform

$$|v_j\rangle = \hat{U}|u_j\rangle, \quad (4.75)$$

and, second,

Unitary
operator's
definition

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{I}. \quad (4.76)$$

(Due to the last property,¹⁶ $\hat{U}$ is called a *unitary operator*, and Eq. (75), a *unitary transformation*.)

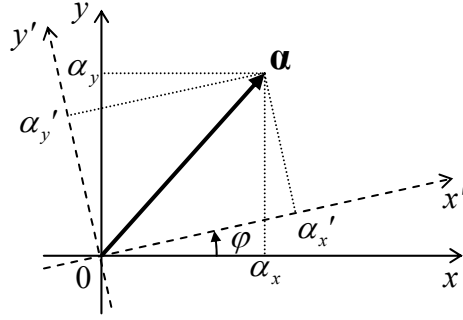


Fig. 4.4. Transformation of components of a 2D vector at a reference frame rotation.

A very simple proof of both statements may be achieved by construction. Indeed, let us take

Unitary
operator
of basis
transform

$$\hat{U} \equiv \sum_{j'} |v_{j'}\rangle \langle u_{j'}|, \quad (4.77)$$

- an evident generalization of Eq. (44). Then

$$\hat{U}|u_j\rangle = \sum_{j'} |v_{j'}\rangle \langle u_{j'}|u_j\rangle = \sum_{j'} |v_{j'}\rangle \delta_{jj'} = |v_j\rangle, \quad (4.78)$$

so that Eq. (75) has been proved. Now, applying Eq. (31) to each term of sum (77), we get

Conjugate
unitary
transform
operator

$$\hat{U}^\dagger \equiv \sum_{j'} |u_{j'}\rangle \langle v_{j'}|, \quad (4.79)$$

so that

$$\hat{U}\hat{U}^\dagger = \sum_{j,j'} |v_j\rangle \langle u_j|u_{j'}\rangle \langle v_{j'}| = \sum_{j,j'} |v_j\rangle \delta_{jj'} \langle v_{j'}| = \sum_j |v_j\rangle \langle v_j|. \quad (4.80)$$

But according to the closure relation (44), the last expression is just the identity operator, q.e.d.¹⁷ (The proof of the second equality in Eq. (76) is absolutely similar.)

As a by-product of our proof, we have also got another important expression (79). It implies, in particular, that while, according to Eq. (77), operator $\hat{U}$ performs the transform from the “old” basis u_j to the “new” basis v_j , its Hermitian adjoint $\hat{U}^\dagger$ performs the reciprocal unitary transform:

Reciprocal
basis
transform

$$\hat{U}^\dagger |v_j\rangle = \sum_{j'} |u_{j'}\rangle \delta_{jj'} = |u_j\rangle. \quad (4.81)$$

¹⁶ An alternative way to express Eq. (76) is to write $\hat{U}^\dagger = \hat{U}^{-1}$, but I will try to avoid this language.

¹⁷ *Quod erat demonstrandum* (Lat.) – what needed to be proved.

Now, let us see how do the matrix elements of the unitary transform operators look like. Generally, as was stated above, operator's elements depend on the basis we calculate them in, so we should be careful - initially. For example, let us calculate the elements in basis $\{u\}$:

$$U_{jj'}|_{in u} \equiv \langle u_j | \hat{U} | u_{j'} \rangle = \langle u_j | \left(\sum_k |v_k\rangle\langle u_k| \right) | u_{j'} \rangle = \langle u_j | v_{j'} \rangle. \quad (4.82)$$

Now performing a similar calculation in basis $\{v\}$, we get

$$U_{jj'}|_{in v} \equiv \langle v_j | \hat{U} | v_{j'} \rangle = \langle v_j | \left(\sum_k |v_k\rangle\langle u_k| \right) | v_{j'} \rangle = \langle u_j | v_{j'} \rangle. \quad (4.83)$$

Surprisingly, the result is the same! This is of course true for the Hermitian conjugate of the unitary transform operator as well:

$$U_{jj'}^\dagger|_{in u} = U_{jj'}^\dagger|_{in v} = \langle v_j | u_{j'} \rangle. \quad (4.84)$$

These expressions may be used, first of all, to rewrite Eq. (75) in a more direct form. Applying the first of Eqs. (41) to state $v_{j'}$ of the “new” basis, we get

$$|v_{j'}\rangle = \sum_j |u_j\rangle\langle u_j|v_{j'}\rangle = \sum_j U_{jj'}|u_j\rangle. \quad (4.85)$$

Similarly, the reciprocal transform is

$$|u_{j'}\rangle = \sum_j |v_j\rangle\langle v_j|u_{j'}\rangle = \sum_j U_{jj'}^\dagger|v_j\rangle. \quad (4.86)$$

Basis
transforms:
matrix
form

These equations are very convenient for applications; we will use them already later in this section.

Next, we may use Eqs. (83), (84) to express the effect of the unitary transform on expansion coefficients (37) of vectors of an arbitrary state α . In the “old” basis $\{u\}$, they are given by Eq. (40). Similarly, in the “new” basis $\{v\}$,

$$\alpha_j|_{in v} = \langle v_j | \alpha \rangle. \quad (4.87)$$

Again inserting the identity operator in the form of closure (44), with internal index j' , and then using Eq. (84), we get

$$\alpha_j|_{in v} = \langle v_j | \left(\sum_{j'} |u_{j'}\rangle\langle u_{j'}| \right) | \alpha \rangle = \sum_{j'} \langle v_j | u_{j'} \rangle \langle u_{j'} | \alpha \rangle = \sum_{j'} U_{jj'}^\dagger \langle u_{j'} | \alpha \rangle = \sum_{j'} U_{jj'}^\dagger \alpha_{j'}|_{in u}. \quad (4.88)$$

The reciprocal transform is (of course) performed by matrix elements of operator $\hat{U}$:

$$\alpha_j|_{in u} = \sum_{j'} U_{jj'} \alpha_{j'}|_{in v}. \quad (4.89)$$

Both structurally and philosophically, these expressions are similar to the transformation of components of a usual vector at coordinate frame rotation. For example, in two dimensions (Fig. 4):

$$\begin{pmatrix} \alpha_x' \\ \alpha_y' \end{pmatrix} = \begin{pmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{pmatrix} \begin{pmatrix} \alpha_x \\ \alpha_y \end{pmatrix}. \quad (4.90)$$

(In this analogy, the equality to 1 of the determinant of the rotation matrix in Eq. (90) corresponds to the unitary property (76) of the unitary transform operators.) Please pay attention here: while the transform (75) from the “old” basis $\{u\}$ to the “new” basis $\{v\}$ is performed by the unitary operator, the change (88) of a state vectors components at this transformation requires its Hermitian conjugate. Actually, this is also natural from the point of view of the geometric analog of the unitary transform (Fig. 4): if the “new” reference frame $\{x', y'\}$ is obtained by a *counterclockwise* rotation of the “old” frame $\{x, y\}$ by some angle φ , for the observer rotating with the frame, vector α (which is itself unchanged) rotates *clockwise*. Due to the analogy between expressions (88) and (89) on one hand, and our old friend Eq. (62) on the other hand, it is tempting to skip indices in our new results by writing

$$|\alpha\rangle_{\text{in } v} = \hat{U}^\dagger |\alpha\rangle_{\text{in } u}, \quad |\alpha\rangle_{\text{in } u} = \hat{U} |\alpha\rangle_{\text{in } v}. \quad (4.91)$$

Since matrix elements of $\hat{U}$ and $\hat{U}^\dagger$ do not depend on basis, such language is not too bad; still, the *symbolic* Eq. (91) should not be confused with *genuine* (basis-independent) bra-ket equalities.

Now let us use the same trick of identity operator insertion, repeated twice, to find the transformation rule for matrix elements of an arbitrary operator:

$$A_{jj'}|_{\text{in } v} \equiv \langle v_j | \hat{A} | v_{j'} \rangle = \langle v_j | \left(\sum_k |u_k\rangle \langle u_k| \right) \hat{A} \left(\sum_{k'} |u_{k'}\rangle \langle u_{k'}| \right) | v_{j'} \rangle = \sum_{k,k'} U_{jk}^\dagger A_{kk'}|_{\text{in } u} U_{k'j'}; \quad (4.92)$$

Matrix
elements'
transforms

absolutely similarly, we can get

$$A_{jj'}|_{\text{in } u} \equiv \sum_{k,k'} U_{jk} A_{kk'}|_{\text{in } v} U_{k'j'}^\dagger. \quad (4.93)$$

In the spirit of Eq. (91), we may present these results symbolically as well, in a compact bra-ket form:

$$\hat{A}|_{\text{in } v} = \hat{U}^\dagger \hat{A}|_{\text{in } u} \hat{U}, \quad \hat{A}|_{\text{in } u} = \hat{U} \hat{A}|_{\text{in } v} \hat{U}^\dagger. \quad (4.94)$$

As a sanity check, let us apply this result to the identity operator:

$$\hat{I}|_{\text{in } v} = \left(\hat{U}^\dagger \hat{I} \hat{U} \right)_{\text{in } u} = \left(\hat{U}^\dagger \hat{U} \right)_{\text{in } u} = \hat{I}|_{\text{in } u} \quad (4.95)$$

- as it should be. One more invariant of the basis change is the *trace* of any operator, defined as the sum of the diagonal terms of its matrix in a certain basis:

$$\text{Tr } \hat{A} \equiv \text{Tr } A \equiv \sum_j A_{jj}. \quad (4.96)$$

Operator/
matrix
trace

The (easy) proof of this fact, using the relations we have already discussed, is left for reader's exercise.

So far, I have implied that both state bases $\{u\}$ and $\{v\}$ are known, and the natural question is where does this information comes from in quantum mechanics of actual physical systems. To get a partial answer to this question, let us return to Eq. (68) that defines eigenstates and eigenvalues of an

operator. Let us assume that the eigenstates a_j of a certain operator $\hat{A}$ form a full and orthonormal set, and find the matrix elements of the operator in the basis of these states. For that, it is sufficient to inner-multiply both sides of Eq. (68), written for index j' , by the bra-vector of an arbitrary state a_j of the same set:

$$\langle a_j | \hat{A} | a_{j'} \rangle = \langle a_j | A_{j'} | a_{j'} \rangle. \quad (4.97)$$

The left-hand part is just the matrix element $A_{jj'}$ we are looking for, while the right hand part is just $A_{j'}\delta_{jj'}$. As a result, we see that the matrix is diagonal, with the diagonal consisting of eigenvalues:

$$A_{jj'} = A_j \delta_{jj'}. \quad (4.98)$$

Matrix
elements in
eigenstate
basis

In particular, in the eigenstate basis (but not necessarily in an arbitrary basis!), A_{jj} means the same as A_j . Thus the most important problem of finding the eigenvalues and eigenstates of an operator is equivalent to the *diagonalization* of its matrix,¹⁸ i.e. finding the basis in which the corresponding operator acquires the diagonal form (98); then the diagonal elements are the eigenvalues, and the basis itself is the desirable set of eigenstates.

Let us modify the above calculation by inner-multiplying Eq. (68) by a bra-vector of a *different* basis – say, the one, denoted $\{u\}$, in which we know the matrix elements $A_{jj'}$. The multiplication gives

$$\langle u_k | \hat{A} | a_j \rangle = \langle u_k | A_j | a_j \rangle. \quad (4.99)$$

In the left-hand part we can (as usual :-)) insert the identity operator, between the operator and the ket-vector, and then use the closure relation (44), while in the right-hand part, we can move the eigenvalue A_j out of the bra-ket, and then insert a summation over a new index, compensating it with the proper Kronecker delta symbol:

$$\langle u_k | \hat{A} \sum_{k'} | u_{k'} \rangle \langle u_{k'} | a_j \rangle = A_j \sum_{k'} \langle u_k | a_j \rangle \delta_{kk'}. \quad (4.100)$$

Moving out the sign of summation over k' , and using definition (47) of the matrix elements, we get

$$\sum_{k'} (A_{kk'} - A_j \delta_{kk'}) \langle u_{k'} | a_j \rangle = 0. \quad (4.101)$$

But the set of such equalities, for all N possible values of index k , is just a system of linear, homogeneous equations for unknown c -numbers $\langle u_k | a_j \rangle$. But according to Eqs. (82)-(84), these numbers are nothing else than the matrix elements U_{kj} of a unitary matrix providing the required transformation from the initial basis $\{u\}$ to the basis $\{a\}$ that diagonalizes matrix A . The system may be presented in the matrix form:

$$\begin{pmatrix} A_{11} - A_j & A_{12} & \dots \\ A_{21} & A_{22} - A_j & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} U_{1j} \\ U_{2j} \\ \dots \end{pmatrix} = 0, \quad (4.102)$$

Operator
diagonal-
ization

¹⁸ Note that expression “matrix diagonalization” is a common and convenient, but dangerous jargon. (A matrix is just a matrix, an ordered set of c -numbers, and cannot be diagonalized.) It is OK to use this jargon if you remember clearly what it actually means – see the definition above.

and the usual condition of its consistency,

Characteristic
equation
for finding
eigenvalues

$$\begin{vmatrix} A_{11} - A_j & A_{12} & \dots \\ A_{21} & A_{22} - A_j & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0, \quad (4.103)$$

plays the role of the characteristic equation of the system. This equation has N roots A_j ; plugging each of them back into system (102), we can use it to find N matrix elements U_{kj} ($k = 1, 2, \dots, N$) corresponding to this particular eigenvalue. However, since equations (103) are homogeneous, they allow finding U_{kj} only to a constant multiplier. In order to ensure their normalization, i.e. the unitary character of matrix U , we may use the condition that all eigenvectors are normalized (just as the basis vectors are):

$$\langle a_j | a_j \rangle = \sum_k \langle a_j | u_k \rangle \langle u_k | a_j \rangle = \sum_k |U_{kj}|^2 = 1, \quad (4.104)$$

for each j . This normalization completes the diagonalization.¹⁹

Now (at last!) I can give the reader some examples. As a simple but very important case, let us diagonalize the operators described (in a certain 2-function basis $\{u\}$) by the so-called *Pauli matrices*

Pauli
matrices

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (4.105)$$

Though introduced by a physicist, with a specific purpose to describe electron's spin, these matrices have a general mathematical significance, because together with the 2×2 identity matrix I , they provide a full, linearly-independent 2×2 basis - meaning that an arbitrary 2×2 matrix may be presented as

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = a_0 I + a_x \sigma_x + a_y \sigma_y + a_z \sigma_z, \quad (4.106)$$

with a unique set of 4 coefficients a .

Let us start with diagonalizing matrix σ_x . For it, the characteristic equation (103) is evidently

$$\begin{vmatrix} -A_j & 1 \\ 1 & -A_j \end{vmatrix} = 0, \quad (4.107)$$

and has two roots, $A_{1,2} = \pm 1$. (Again, the numbering is arbitrary!) The reader may readily check that the eigenvalues of matrices σ_y and σ_z are similar. However, the eigenvectors of the operators corresponding to all these matrices are different. To find them for σ_x , let us plug its first eigenvalue, $A_1 = +1$, back into equations (101), written for this particular case:

$$\begin{aligned} -\langle u_1 | a_1 \rangle + \langle u_2 | a_1 \rangle &= 0, \\ \langle u_1 | a_1 \rangle - \langle u_2 | a_1 \rangle &= 0. \end{aligned} \quad (4.108)$$

¹⁹ A possible slight complication here are degenerate cases when characteristic equation gives certain equal eigenvalues corresponding to different eigenvectors. In this case the requirement of the mutual orthogonality of these states should be additionally enforced.

The equations are compatible (of course, because the used eigenvalue $A_1 = +1$ satisfies the characteristic equation), and any of them gives

$$\langle u_1 | a_1 \rangle = \langle u_2 | a_1 \rangle, \quad \text{i.e.} \quad U_{11} = U_{21}. \quad (4.109)$$

With that, the normalization condition (104) yields

$$|U_{11}|^2 = |U_{21}|^2 = \frac{1}{2}. \quad (4.110)$$

Although the normalization is insensitive to the simultaneous multiplication of U_{11} and U_{21} by the same phase factor $\exp\{i\varphi\}$ with any real φ , it is convenient to keep the coefficients real, for example taking $\varphi = 0$, i.e. to get

$$U_{11} = U_{21} = \frac{1}{\sqrt{2}}. \quad (4.111)$$

Performing an absolutely similar calculation for the second characteristic value, $A_2 = -1$, we get $U_{12} = -U_{22}$, and we may choose the common phase to get

$$U_{12} = -U_{22} = \frac{1}{\sqrt{2}}, \quad (4.112)$$

so that the whole unitary matrix for diagonalization of the operator corresponding to σ_x is²⁰

$$U_x = U_x^\dagger = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \quad (4.113)$$

Unitary
matrix
diagonalizing
 σ_x

For what follows, it will be convenient to have this result expressed in the ket-relation form – see Eqs. (85)-(86):

$$|a_1\rangle = U_{11}|u_1\rangle + U_{21}|u_2\rangle = \frac{1}{\sqrt{2}}(|u_1\rangle + |u_2\rangle), \quad |a_2\rangle = U_{12}|u_1\rangle + U_{22}|u_2\rangle = \frac{1}{\sqrt{2}}(|u_1\rangle - |u_2\rangle), \quad (4.114)$$

$$|u_1\rangle = U_{11}^\dagger|a_1\rangle + U_{21}^\dagger|a_2\rangle = \frac{1}{\sqrt{2}}(|a_1\rangle + |a_2\rangle), \quad |u_2\rangle = U_{12}^\dagger|a_1\rangle + U_{22}^\dagger|a_2\rangle = \frac{1}{\sqrt{2}}(|a_1\rangle - |a_2\rangle), \quad (4.115)$$

These results are already sufficient to understand the Stern-Gerlach experiments described in Sec. 1 - with two additional postulates. The first of them is that particle's interaction with external magnetic field may be described by the following vector operator of the dipole magnetic moment:²¹

$$\hat{\mathbf{m}} = \gamma \hat{\mathbf{S}}, \quad (4.116)$$

Magnetic
moment
operator

where the coefficient γ , specific for every particle type, is called the *gyromagnetic ratio*,²² and $\hat{\mathbf{S}}$ is the vector operator of spin. For the so-called *spin-1/2 particles* (including the electron), this operator may be represented, in the so-called *z-basis*, by the following 3D vector of the Pauli matrices (105):

²⁰ Note that though this particular unitary matrix is Hermitian, this is not true for an arbitrary choice of phases φ .

²¹ This is the key point in the electron's spin description, developed by W. Pauli in 1925-1927.

²² For an electron, with its negative charge $q = -e$, the gyromagnetic ratio is negative: $\gamma_e = -g_e e / 2m_e$, where $g_e \approx 2$ is the dimensionless *g-factor*. Due to quantum electrodynamics effects, the factor is slightly higher than 2: $g_e = 2(1 + \alpha/2\pi + \dots) \approx 2.002319304\dots$, where $\alpha \equiv e^2/4\pi\epsilon_0\hbar c \approx 1/137$ is the *fine structure* ("Sommerfeld") *constant*.

Spin-1/2
matrix

$$\mathbf{S} = \frac{\hbar}{2}(\mathbf{n}_x \sigma_x + \mathbf{n}_y \sigma_y + \mathbf{n}_z \sigma_z) = \frac{\hbar}{2} \begin{pmatrix} \mathbf{n}_z & \mathbf{n}_x - i\mathbf{n}_y \\ \mathbf{n}_x + i\mathbf{n}_y & -\mathbf{n}_z \end{pmatrix}, \quad (4.117)$$

and $\mathbf{n}_{x,y,z}$ are the usual Cartesian unit vectors in 3D space. (In the quantum-mechanics sense, they are just *c*-numbers, or rather “*c*-vectors”.) The *z*-basis, in which Eq. (177) is valid, is *defined* as an orthonormal basis of two states, frequently denoted $\uparrow$ and $\downarrow$, in which the *z*-component of the vector operator of spin is diagonal, with eigenvalues $+\hbar/2$ and $-\hbar/2$. Note that we do not “understand” what exactly these states are,²³ but loosely associate them with a certain internal rotation of the electron about *z*-axis, with either positive or negative angular momentum component S_z . However, any attempt to use such classical interpretation for quantitative predictions runs into fundamental difficulties – see Sec. 5.7 below.

The second new postulate describes the general relation between the bra-ket formalism and experiment.²⁴ Namely, in quantum mechanics, each real observable A is represented by a Hermitian operator $\hat{A} = \hat{A}^\dagger$, and a result of its measurement in a quantum state α , described by a linear superposition of the eigenstates a_j of the operator,

$$|\alpha\rangle = \sum_j \alpha_j |a_j\rangle, \quad \text{with } \alpha_j = \langle a_j | \alpha \rangle, \quad (4.118)$$

may be only one of corresponding eigenvalues A_j .²⁵ If state (118) and all eigenstates α_j are normalized to unity,

$$\langle \alpha | \alpha \rangle = 1, \quad \langle a_j | a_j \rangle = 1, \quad (4.119)$$

then the probability of outcome A_j is²⁶

$$W_j = |\alpha_j|^2 = \alpha_j^* \alpha_j = \langle \alpha | a_j \rangle \langle a_j | \alpha \rangle, \quad (4.120)$$

This relation is evidently a generalization of Eq. (1.22) in wave mechanics. As a sanity check, let us assume that the set of eigenstates a_j is full, and calculate the sum of all the probabilities:

$$\sum_j W_j = \sum_j \langle \alpha | a_j \rangle \langle a_j | \alpha \rangle = \langle \alpha | \hat{I} | \alpha \rangle = 1. \quad (4.121)$$

Now returning to the Stern-Gerlach experiment, conceptually the description of the first (*z*-oriented) experiment shown in Fig. 1 is the hardest for us, because the statistical ensemble describing the unpolarized electron beam at its input is *mixed* (“incoherent”), and cannot be described by a *pure*

²³ If you think about it, word “understand” typically means that we can explain a new, more complex notion in terms of those discussed earlier and considered “known”. In our example, we cannot express the spin states by some wavefunction $\psi(\mathbf{r})$, or any other mathematical notion discussed earlier. The bra-ket formalism has been invented exactly to enable mathematical analysis of such “new” quantum states.

²⁴ Here again, just like in Sec. 1.2, the statement implies the abstract (mathematical) notion of “ideal experiments”, postponing the discussion of real (physical) measurements until Sec. 7.7.

²⁵ As a reminder, in the end of Sec. 3 we have already proved that such eigenstates corresponding to different A_j are orthogonal. If any of these values is degenerate, i.e. corresponds to several different eigenstates, they should be also selected orthogonal, in order for Eq. (118) to be valid.

²⁶ This key relation, in particular, explains the most common term for the (generally, complex) coefficients α_j , the *probability amplitudes*.

Quantum
measurement
postulate

(“coherent”) superposition of the type (6) that have been the subject of our studies so far. (We will discuss the mixed ensembles in Chapter 7.) However, it is intuitively clear that its results, and in particular Eq. (6), are compatible with the description of its two output beams as sets of electrons in pure states $\uparrow$ and $\downarrow$, respectively. The absorber following that first stage (Fig. 2) just takes all spin-down electrons out of the picture, producing an output beam of polarized electrons in a pure $\uparrow$ state. For such beam, probabilities (120) are $W_{\uparrow} = 1$ and $W_{\downarrow} = 0$. This is certainly compatible with the result of the “control” experiment shown on the bottom panel of Fig. 2: the repeated SG (z) stage does not split such a beam, keeping the probabilities the same.

Now let us discuss the double Stern-Gerlach experiment shown on the top panel of Fig. 2. For that, let us present the z -polarized beam in another basis of two states (I will denote them as $\rightarrow$ and $\leftarrow$) in which, by definition, the matrix of operator $\hat{S}_x$ is diagonal. But this is exactly the set we called $a_{1,2}$ in the σ_x matrix diagonalization problem solved above. On the other hand, states $\uparrow$ and $\downarrow$ are exactly what we called $u_{1,2}$ in that problem, because in this basis, matrices σ_z and hence S_z are diagonal. Hence, in application to the electron spin problem, we may rewrite Eqs. (114)-(115) as

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle), \quad |\leftarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle), \quad (4.122)$$

$$|\uparrow\rangle = \frac{1}{\sqrt{2}}(|\rightarrow\rangle + |\leftarrow\rangle), \quad |\downarrow\rangle = \frac{1}{\sqrt{2}}(|\rightarrow\rangle - |\leftarrow\rangle), \quad (4.123)$$

Relation
between
eigenvectors
of operators
 S_x and S_z

Currently, for us the first of Eqs. (123) is most important, because it shows that the quantum state of electrons entering the SG (x) stage may be presented as a coherent superposition of electrons with $S_x = +\hbar/2$ and $S_x = -\hbar/2$. Notice that the beams have equal probability amplitude moduli, so that according to Eq. (122), the split beams $\rightarrow$ and $\leftarrow$ have equal intensities, in accordance with experiment. (The minus sign before the second ket-vector is of no consequence here, though it may have an impact on outcome of other experiments – for example if the $\rightarrow$ and $\leftarrow$ beams are brought together again.)

Now, let us discuss the most mysterious (from the classical point of view) multi-stage SG experiment shown on the middle panel of Fig. 2. After the second absorber has taken out all electrons in, say, the $\leftarrow$ state, the remaining electrons in state $\rightarrow$ are passed to the final, SG (z), stage. But according to the first of Eqs. (122), this state may be presented as a (coherent) linear superposition of the $\uparrow$ and $\downarrow$ states, with equal amplitudes. The stage separates these two states into separate beams, with equal probabilities $W_{\uparrow} = W_{\downarrow} = 1/2$ to find an electron in each of them, thus explaining the experimental results.

To conclude our discussion of the multistage Stern-Gerlach experiment, let me note that though it cannot be explained in terms of wave mechanics (which operates with *scalar* de Broglie waves), it has an analogy in classical theories of *vector* fields, such as the classical electrodynamics. Let a plane electromagnetic wave propagate perpendicular to the plane of drawing, and pass through linear polarizer 1. Similarly to the initial SG (z) stages (including the following absorbers) shown in Fig. 2, the polarizer produces a wave linearly polarized in one direction – the vertical direction in Fig. 3. Its electric field vector has no horizontal component, as may be revealed by wave’s full absorption in a perpendicular polarizer 3. However, let us pass the wave through polarizer 2 first. In this case, the output wave does acquire a horizontal component, as can be, again, revealed by passing it through polarizer 3. If angles between polarization direction 1 and 2, and between 2 and 3, are both equal $\pi/4$, each polarizer reduces the wave amplitude by a factor of $\sqrt{2}$, and hence intensity by a factor of 2, exactly like in the multistage

SG experiment, with polarizer 2 playing the role of the SG (x) stage. The “only” difference is that the necessary angle is $\pi/4$, rather than by $\pi/2$ for the Stern-Gerlach experiment. In quantum electrodynamics (see Chapter 9 below), which confirms the classical predictions for this experiment, this difference is explained by that between the *integer* spin of the electromagnetic field quanta, photons, and the *half-integer* spin of electrons.

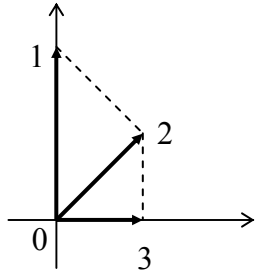


Fig. 4.3. Light polarization sequence similar to the 3-stage Stern-Gerlach experiment shown on the middle panel of Fig. 2.

4.5. Observables: Expectation values and uncertainties

After this particular (and hopefully expiring) example, let us discuss the general relation between the Dirac formalism and experiment in more detail. The expectation value of an observable over *any* statistical ensemble (not necessarily coherent) may be always calculated using the general rule (1.37). For the particular case of a coherent superposition (118), we can combine that definition with Eq. (120) and the second of Eqs. (118), and then use Eqs. (59) and (98) to write

$$\langle A \rangle = \sum_j A_j W_j = \sum_j \alpha_j^* A_j \alpha_j = \sum_j \langle \alpha | a_j \rangle A_j \langle a_j | \alpha \rangle = \sum_{j,j'} \langle \alpha | a_j \rangle \langle a_j | \hat{A} | a_{j'} \rangle \langle a_{j'} | \alpha \rangle. \quad (4.124)$$

Now using the completeness relation (44) twice, with indices j and j' , we arrive at a very simple and important formula²⁷

$$\langle A \rangle = \langle \alpha | \hat{A} | \alpha \rangle. \quad (4.125)$$

Expectation
value
as a long
bracket

This is a clear analog of the wave-mechanics formula (1.23) – and as we will see in the next chapter, may be used to derive it. A huge advantage of Eq. (125) is that it does not explicitly involve the eigenvector set of the corresponding operator, and allows the calculation to be performed in any convenient basis.²⁸

For example, let us consider an arbitrary state α of spin- $1/2$, and calculate the expectation values of its components. The calculations are easiest in the z -basis, because we know the operators of the components in that basis – see Eq. (117). Representing the ket- and bra-vectors of our state as linear superpositions of vectors of the basis states $\uparrow$ and $\downarrow$,

$$|\alpha\rangle = \alpha_\uparrow |\uparrow\rangle + \alpha_\downarrow |\downarrow\rangle, \quad \langle\alpha| = \langle\uparrow| \alpha_\uparrow^* + \langle\downarrow| \alpha_\downarrow^*. \quad (4.126)$$

²⁷ This equality reveals the full beauty of Dirac’s notation. Indeed, initially the quantum-mechanical brackets just *reminded* the angular brackets used for statistical averaging. Now we see that in this particular (but most important) case, the angular brackets of these two types may be indeed *equal* to each other!

²⁸ Note that Eq. (120) may be rewritten in the form similar to Eq. (125): $W_j = \langle \alpha | \hat{\Lambda}_j | \alpha \rangle$, where $\hat{\Lambda}_j \equiv |a_j\rangle\langle a_j|$ is the operator (42) of projection upon the j^{th} eigenstate a_j .

and plugging these expressions to Eq. (125) written for observable S_z , we get

$$\begin{aligned}\langle S_z \rangle &= \left(\langle \uparrow | \alpha_{\uparrow}^* + \langle \downarrow | \alpha_{\downarrow}^* \right) \hat{S}_z \left(\alpha_{\uparrow} | \uparrow \rangle + \alpha_{\downarrow} | \downarrow \rangle \right) \\ &= \alpha_{\uparrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_z | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_z | \downarrow \rangle + \alpha_{\uparrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_z | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_z | \downarrow \rangle.\end{aligned}\quad (4.127)$$

Now there are two equivalent ways (both very simple :-) to calculate the bra-kets in this expression. The first one is to represent each of them in the matrix form in the z -basis, in which bra- and ket-vectors of states $\uparrow$ and $\downarrow$ are, respectively, matrix-rows (1, 0) and (0, 1), or the similar matrix-columns. Another (perhaps more elegant) way is to use the general Eq. (59), for the z -basis, to write

$$\hat{S}_x = \frac{\hbar}{2} (|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|), \quad \hat{S}_y = -i \frac{\hbar}{2} (|\uparrow\rangle\langle\downarrow| - |\downarrow\rangle\langle\uparrow|), \quad \hat{S}_z = \frac{\hbar}{2} (|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|). \quad (4.128)$$

Spin-1/2
component
operators

For our particular calculation, we may plug the last of these expressions into Eq. (127), and to use the orthonormality conditions (119):

$$\langle \uparrow | \uparrow \rangle = \langle \downarrow | \downarrow \rangle = 1, \quad \langle \uparrow | \downarrow \rangle = \langle \downarrow | \uparrow \rangle = 0. \quad (4.129)$$

Both calculations give (of course) the same result:

$$\langle S_z \rangle = \frac{\hbar}{2} (\alpha_{\uparrow} \alpha_{\uparrow}^* - \alpha_{\downarrow} \alpha_{\downarrow}^*). \quad (4.130)$$

This particular result might be also obtained using Eq. (120) for probabilities $W_{\uparrow} = \alpha_{\uparrow} \alpha_{\uparrow}^*$ and $W_{\downarrow} = \alpha_{\downarrow} \alpha_{\downarrow}^*$:

$$\langle S_z \rangle = W_{\uparrow} \left(+ \frac{\hbar}{2} \right) + W_{\downarrow} \left(- \frac{\hbar}{2} \right) = \alpha_{\uparrow} \alpha_{\uparrow}^* \left(+ \frac{\hbar}{2} \right) + \alpha_{\downarrow} \alpha_{\downarrow}^* \left(- \frac{\hbar}{2} \right). \quad (4.131)$$

The formal way (127), based on using Eq. (125), has, however, an advantage of being applicable, without any change, to finding the observables whose operators are not diagonal in the z -basis, as well. In particular, absolutely similar calculations give

$$\langle S_x \rangle = \alpha_{\uparrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_x | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_x | \downarrow \rangle + \alpha_{\uparrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_x | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_x | \downarrow \rangle = \frac{\hbar}{2} (\alpha_{\uparrow} \alpha_{\downarrow}^* + \alpha_{\downarrow} \alpha_{\uparrow}^*), \quad (4.132)$$

$$\langle S_y \rangle = \alpha_{\uparrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_y | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_y | \downarrow \rangle + \alpha_{\uparrow} \alpha_{\downarrow}^* \langle \downarrow | \hat{S}_y | \uparrow \rangle + \alpha_{\downarrow} \alpha_{\uparrow}^* \langle \uparrow | \hat{S}_y | \downarrow \rangle = i \frac{\hbar}{2} (\alpha_{\uparrow} \alpha_{\downarrow}^* - \alpha_{\downarrow} \alpha_{\uparrow}^*), \quad (4.133)$$

Similarly, we can express, via the same coefficients $\alpha_{\uparrow}$ and $\alpha_{\downarrow}$, the r.m.s. fluctuations of all spin components. For example, let us have a good look at the spin state $\uparrow$. According to Eq. (126), in this state $\alpha_{\uparrow} = 1$ and $\alpha_{\downarrow} = 0$, so that Eqs. (130)-(133) yield:

$$\langle S_z \rangle = \frac{\hbar}{2}, \quad \langle S_x \rangle = \langle S_y \rangle = 0. \quad (4.134)$$

Now let us use the same Eq. (125) to calculate the spin component uncertainties. According to Eqs. (105) and (117), operators of spin component squared are equal to $(\hbar/2)^2 \hat{I}$, so that the general Eq. (1.33) yields

$$(\delta S_z)^2 = \langle S_z^2 \rangle - \langle S_z \rangle^2 = \langle \uparrow | \hat{S}_z^2 | \uparrow \rangle - \left(\frac{\hbar}{2} \right)^2 = \left(\frac{\hbar}{2} \right)^2 \langle \uparrow | \hat{I} | \uparrow \rangle - \left(\frac{\hbar}{2} \right)^2 = 0, \quad (4.135a)$$

$$(\delta S_x)^2 = \langle S_x^2 \rangle - \langle S_x \rangle^2 = \langle \uparrow | \hat{S}_x^2 | \uparrow \rangle - 0 = \left(\frac{\hbar}{2} \right)^2 \langle \uparrow | \hat{I} | \uparrow \rangle = \left(\frac{\hbar}{2} \right)^2, \quad (4.135b)$$

$$(\delta S_y)^2 = \langle S_y^2 \rangle - \langle S_y \rangle^2 = \langle \uparrow | \hat{S}_y^2 | \uparrow \rangle - 0 = \left(\frac{\hbar}{2} \right)^2 \langle \uparrow | \hat{I} | \uparrow \rangle = \left(\frac{\hbar}{2} \right)^2. \quad (4.135c)$$

While Eqs. (134) and (135a) are compatible with the classical notion of the spin being “definitely in the $\uparrow$ state”, this correspondence should not be overstretched to the interpretation of this state as a certain (z) orientation of electron’s magnetic moment $\mathbf{m}$, because such classical picture cannot explain Eqs. (135b) and (135c). The best (but still imprecise!) classical image I can offer is the magnetic moment $\mathbf{m}$ oriented, on the average, in the z -direction, but still having x - and y -components strongly “wobbling” about their zero average values.

It is straightforward to verify that in the x -polarized and y -polarized states the situation is similar, with the corresponding change of indices. Thus, in neither state may all 3 components of the spin have exact values. Let me show that this is not just an occasional fact, but reflects the most profound property of quantum mechanics, the *uncertainty relations*. Consider 2 observables, A and B , that may be measured in the same quantum state. There are two possibilities here. If operators corresponding to the observables commute,

$$[\hat{A}, \hat{B}] = 0, \quad (4.136)$$

then all the matrix elements of the commutator in any orthogonal basis (in particular, in the basis of eigenstates a_j of operator A) are also zero. From here, we get

$$\langle a_j | [\hat{A}, \hat{B}] | a_{j'} \rangle = \langle a_j | \hat{A} \hat{B} | a_{j'} \rangle - \langle a_j | \hat{B} \hat{A} | a_{j'} \rangle = 0. \quad (4.137)$$

In the first bra-ket of the middle expression, let us act by operator $\hat{A}$ on the bra-vector, while in the second one, on the ket-vector. According to Eq. (68), such action turns operators into the corresponding eigenvalues, so that we get

$$A_j \langle a_j | \hat{B} | a_{j'} \rangle - A_{j'} \langle a_j | \hat{B} | a_{j'} \rangle = (A_j - A_{j'}) \langle a_j | \hat{B} | a_{j'} \rangle = 0. \quad (4.138)$$

This means that if eigenstates of operator $\hat{A}$ are non-degenerate (i.e. $A_j \neq A_{j'}$ if $j \neq j'$), the matrix of operator $\hat{B}$ has to be diagonal in basis a_j , i.e., the eigenstate sets of operators $\hat{A}$ and $\hat{B}$ coincide. Such pairs of observables, that share their eigenstates, are called *compatible*. For example, in wave mechanics of a particle, momentum (1.26) and the kinetic energy (1.27) are compatible, sharing eigenfunctions (1.29). Now we see that this is not occasional, because each Cartesian component of the kinetic energy is proportional to the square of the corresponding component of the momentum, and any operator commutes with an arbitrary power of itself:

$$[\hat{A}, \hat{A}^n] \equiv \left[\hat{A}, \underbrace{\hat{A} \hat{A} \dots \hat{A}}_n \right] = \hat{A} \underbrace{\hat{A} \hat{A} \dots \hat{A}}_n - \underbrace{\hat{A} \hat{A} \dots \hat{A}}_n \hat{A} = 0. \quad (4.139)$$

Now, what if operators $\hat{A}$ and $\hat{B}$ do *not* commute? Then the following *general uncertainty relation* is valid:²⁹

$$\delta A \delta B \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|. \quad (4.140) \quad \text{General uncertainty relation}$$

The proof of Eq. (140) may be divided into two steps, the first of which proves the so-called *Schwartz inequality*:³⁰

$$\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle \geq \left| \langle \alpha | \beta \rangle \right|^2. \quad (4.141) \quad \text{Schwartz inequality}$$

The proof may be started by using postulate (16) - that the norm of any legitimate state of the system cannot be negative. Let us apply this postulate to the state with the following ket-vector:

$$|\delta\rangle \equiv |\alpha\rangle - \frac{\langle \beta | \alpha \rangle}{\langle \beta | \beta \rangle} |\beta\rangle, \quad (4.142)$$

where α and β are possible, non-null states of the system, so that the denominator in Eq. (142) is not equal to zero. For this case, Eq. (16) gives

$$\left(\langle \alpha | - \frac{\langle \alpha | \beta \rangle}{\langle \beta | \beta \rangle} \langle \beta | \right) \left(|\alpha\rangle - \frac{\langle \beta | \alpha \rangle}{\langle \beta | \beta \rangle} |\beta\rangle \right) \geq 0. \quad (4.143)$$

Opening the parentheses, we get

$$\langle \alpha | \alpha \rangle - \frac{\langle \alpha | \beta \rangle}{\langle \beta | \beta \rangle} \langle \beta | \alpha \rangle - \frac{\langle \beta | \alpha \rangle}{\langle \beta | \beta \rangle} \langle \alpha | \beta \rangle + \frac{\langle \alpha | \beta \rangle \langle \beta | \alpha \rangle}{\langle \beta | \beta \rangle^2} \langle \beta | \beta \rangle \geq 0. \quad (4.144)$$

After the cancellation of one inner product $\langle \beta | \beta \rangle$ in the nominator and denominator of the last term, it cancels with the 2nd (or 3rd) term, proving the Schwartz inequality (141).

Now let us apply this inequality to states

$$|\alpha\rangle \equiv \hat{A}|\gamma\rangle \quad \text{and} \quad |\beta\rangle \equiv \hat{B}|\gamma\rangle, \quad (4.145)$$

where, in both relations, γ is the same (but otherwise arbitrary) possible state of the system, and the deviations operators are defined similarly to observable deviations (see Sec. 1.2), for example,

$$\hat{\tilde{A}} \equiv \hat{A} - \langle A \rangle. \quad (4.146)$$

With this substitution, and taking into account that the observable operators $\hat{A}$ and $\hat{B}$ are Hermitian, Eq. (141) yields

$$\langle \gamma | \hat{\tilde{A}}^2 | \gamma \rangle \langle \gamma | \hat{\tilde{B}}^2 | \gamma \rangle \geq \left| \langle \gamma | \hat{\tilde{A}} \hat{\tilde{B}} | \gamma \rangle \right|^2. \quad (4.147)$$

²⁹ Note that both sides of Eq. (140) are state-specific; the uncertainty relation statement is that this inequality should be valid for *any* possible quantum state of the system.

³⁰ This inequality is the quantum-mechanical analog of the usual vector algebra result $\alpha^2 \beta^2 \geq |\alpha \cdot \beta|^2$.

Since state γ is arbitrary, we may use Eq. (125) to rewrite this relation as an operator inequality:

$$\delta A \delta B \geq \left| \left\langle \hat{\tilde{A}} \hat{\tilde{B}} \right\rangle \right|. \quad (4.148)$$

Actually, this is already an uncertainty relation, even “better” (stronger) than its standard form (140); moreover, it is more convenient in some cases. In order to proceed to Eq. (140), we need a couple more steps. First, let us notice that the operator product in Eq. (148) may be recast as

$$\hat{\tilde{A}} \hat{\tilde{B}} = \frac{1}{2} \left\{ \hat{\tilde{A}}, \hat{\tilde{B}} \right\} - \frac{i}{2} \hat{C}, \quad \text{where } \hat{C} \equiv i \left[\hat{\tilde{A}}, \hat{\tilde{B}} \right]. \quad (4.149)$$

Any anticommutator of Hermitian operators, including that in Eq. (149), is a Hermitian operator, and its eigenvalues are purely real, so that its expectation value (in any state) is also purely real. On the other hand, the commutator part of Eq. (149) is just

$$\hat{C} \equiv i \left[\hat{\tilde{A}}, \hat{\tilde{B}} \right] = i (\hat{A} - \langle A \rangle) (\hat{B} - \langle B \rangle) - i (\hat{B} - \langle B \rangle) (\hat{A} - \langle A \rangle) = i (\hat{A} \hat{B} - \hat{B} \hat{A}) = i [\hat{A}, \hat{B}]. \quad (4.150)$$

Second, according to Eqs. (52) and (65), the Hermitian conjugate of any product of Hermitian operators $\hat{A}$ and $\hat{B}$ is just the product of swapped operators. Using the fact, we may write

$$\hat{C}^\dagger = (i [\hat{A}, \hat{B}])^\dagger = -i (\hat{A} \hat{B})^\dagger + i (\hat{B} \hat{A})^\dagger = -i \hat{B} \hat{A} + i \hat{A} \hat{B} = i [\hat{A}, \hat{B}] = \hat{C}, \quad (4.151)$$

so that operator $\hat{C}$ is also Hermitian, i.e. its eigenvalues are also real, and thus its average is purely real as well. As a result, the square of the average of the operator product (149) may be presented as

$$\left\langle \hat{\tilde{A}} \hat{\tilde{B}} \right\rangle^2 = \left\langle \frac{1}{2} \left\{ \hat{\tilde{A}}, \hat{\tilde{B}} \right\} \right\rangle^2 + \left\langle \frac{1}{2} \hat{C} \right\rangle^2. \quad (4.152)$$

Since the first term in the right-hand part of this equality cannot be negative,

$$\left\langle \hat{\tilde{A}} \hat{\tilde{B}} \right\rangle^2 \geq \left\langle \frac{1}{2} \hat{C} \right\rangle^2 = \left\langle \frac{i}{2} [\hat{A}, \hat{B}] \right\rangle^2, \quad (4.153)$$

and we can continue Eq. (148) as

$$\delta A \delta B \geq \left| \left\langle \hat{\tilde{A}} \hat{\tilde{B}} \right\rangle \right| \geq \frac{1}{2} \left| \left\langle [\hat{A}, \hat{B}] \right\rangle \right|, \quad (4.154)$$

thus proving Eq. (140).

For the particular case of operators $\hat{x}$ and $\hat{p}_x$ (or a similar pair of operators for another Cartesian coordinate), we can readily combine Eq. (140) with Eq. (2.14b) and to prove the original Heisenberg’s uncertainty relation (2.13). For the spin-1/2 operators defined by Eq. (117), it is straightforward (and highly recommended to the reader) to show that

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z, \quad (4.155)$$

with similar relations for other pairs of indices taken in the “correct” order (from x to y to z to x , etc.). As a result, the uncertainty relations (140) for spin-1/2 particles, notably including electrons, are

Commutation
relation
for spin-1/2
component
operators

$$\delta S_x \delta S_y \geq \frac{\hbar}{2} |\langle S_z \rangle|, \text{ etc.} \quad (4.156)$$

Uncertainty
relations
for spin-1/2
components

In particular, in the $\uparrow$ state, the right-hand part of this relation equals $(\hbar/2)^2$, and neither of the uncertainties δS_x , δS_y can equal zero. As a reminder, our direct calculation earlier in this section has shown that each of these uncertainties is equal to $\hbar/2$, i.e. their product equals to the *lowest* value allowed by the uncertainty relation (156). In this aspect, the spin-polarized states are similar to the Gaussian wave packets studied in Sec. 2.2.

4.6. Quantum dynamics: Three pictures

So far in this chapter, I shied away from the discussion of system dynamics, implying that the bra- and ket-vectors of the system are their “snapshots” at a certain instant t . Now we are sufficiently prepared to examine their time dependence. One of the most beautiful features of quantum mechanics is that the time evolution may be described using either of three alternative “pictures”, giving exactly the same final results for expectation values of all observables.

From the standpoint of our wave mechanics experience, the *Schrödinger picture* is the most natural. In this picture, the operators corresponding to time-independent observables (e.g., to the Hamiltonian function H of an isolated system) are also constant, while the bra- and ket-vectors of the quantum state of the system evolve in time as

$$\langle \alpha(t) | = \langle \alpha(t_0) | \hat{u}^\dagger(t, t_0), \quad | \alpha(t) \rangle = \hat{u}(t, t_0) | \alpha(t_0) \rangle, \quad (4.157)$$

Schrödinger
equation of
operator
evolution

where $\hat{u}(t, t_0)$ is the *time-evolution operator*, which obeys the following differential equation:

$$i\hbar \dot{\hat{u}} = \hat{H} \hat{u}, \quad (4.158)$$

where $\hat{H}$ is the Hamiltonian operator of the system (that is always Hermitian, $\hat{H}^\dagger = \hat{H}$), and the dot means the differentiation is over argument t , but not t_0 . While this equation is a very natural replacement of the wave-mechanical equation (1.25), and is also frequently called the *Schrödinger equation*,³¹ it still should be considered as a new, more general postulate, which finds its final justification (as it is usual in physics) in the agreement between its corollaries with experiment - more exactly, in having not a single credible contradiction with experiment.

Starting the discussion of Eqs. (157)-(158), let us first consider the case of a system described by a time-independent Hamiltonian, whose eigenstates a_n and eigenvalues E_n obey Eq. (68),³²

$$\hat{H} | a_n \rangle = E_n | a_n \rangle, \quad (4.159)$$

and hence are also time-independent. (Similarly to the wavefunctions ψ_n defined by Eq. (1.60), a_n are called the *stationary states* of the system.) Let us use Eqs. (157)-(159) to calculate the law of time evolution of the expansion coefficients α_n , defined by Eq. (118), in the stationary state basis:

³¹ Moreover, we will be able to *derive* Eq. (1.25) from Eq. (154) – see Sec. 5.2.

³² Here I intentionally use index n rather than j to emphasize the special role played by the special role of the stationary eigenstates a_n in quantum dynamics.

$$\begin{aligned}
\dot{\alpha}_n(t) &= \frac{d}{dt} \langle a_n | \alpha(t) \rangle = \frac{d}{dt} \langle a_n | \hat{u}(t, t_0) | \alpha(t_0) \rangle = \langle a_n | \dot{\hat{u}}(t, t_0) | \alpha(t_0) \rangle \\
&= \langle a_n | \frac{1}{i\hbar} \hat{H} \hat{u}(t, t_0) | \alpha(t_0) \rangle = \frac{E_n}{i\hbar} \langle a_n | \hat{u}(t, t_0) | \alpha(t_0) \rangle = \frac{E_n}{i\hbar} \langle a_n | \alpha(t) \rangle = -\frac{i}{\hbar} E_n \alpha_n.
\end{aligned} \tag{4.160}$$

This is the same simple equation as Eq. (1.59), and its integration yields a similar result – cf. Eq. (1.61), just with the initial time t_0 rather than 0:

$$\alpha_n(t) = \alpha_n(t_0) \exp \left\{ -\frac{i}{\hbar} E_n (t - t_0) \right\}. \tag{4.161}$$

Time
evolution
of stationary
states

In order to illustrate how does this result work, let us consider spin- $1/2$ dynamics in a time-independent, uniform external magnetic field $\mathcal{B}$, taking its direction for axis z . To construct the system's Hamiltonian, we may apply the correspondence principle to the classical expression for the energy of a magnetic moment $\mathbf{m}$ in the external magnetic field $\mathcal{B}$,³³

$$U = -\mathbf{m} \cdot \mathcal{B}. \tag{4.162}$$

In quantum mechanics, the operator corresponding to the moment $\mathbf{m}$ is given by Eq. (1.16) (suggested by W. Pauli), so that the spin-field interaction is described by the so-called *Pauli Hamiltonian*:

$$\hat{H} = -\hat{\mathbf{m}} \cdot \mathcal{B} = -\gamma \hat{\mathbf{S}} \cdot \mathcal{B} = -\gamma \mathcal{B} \hat{S}_z, \tag{4.163}$$

Pauli
Hamiltonian:
operator

where $\hat{S}_z$ is the operator of the z -component of electron's spin. According to Eq. (1.17), in the z -basis of states $\uparrow$ and $\downarrow$, the matrix of operator (163) is

$$H = -\frac{\gamma \hbar \mathcal{B}}{2} \sigma_z = -\frac{\hbar \Omega}{2} \sigma_z, \quad \text{with } \Omega \equiv \gamma \mathcal{B}. \tag{4.164}$$

Pauli
Hamiltonian:
 z -basis matrix

The constant Ω so defined coincides with the classical frequency of the precession of a symmetric top, with an angular momentum $\mathbf{S}$ and magnetic moment $\mathbf{m} = \gamma \mathbf{S}$, about axis z , induced by external torque $\boldsymbol{\tau} = \mathbf{m} \times \mathcal{B}$.³⁴

$$\Omega = \frac{\tau}{S} = \frac{m \mathcal{B}}{S} = \gamma \mathcal{B}. \tag{4.165a}$$

For an electron, with its negative gyromagnetic ratio $\gamma_e = -ge/2m_e$, neglecting the minor difference between factors g_e and 2, we get

$$\Omega = -\frac{e}{m_e} \mathcal{B}, \tag{4.165b}$$

i.e. the frequency's magnitude coincides with that of the cyclotron frequency ω_c – see Eq. (3.48).

In order to apply the general Eq. (161), at this stage we would need to find the eigenstates a_n and eigenenergies E_n of our Hamiltonian. However, with our (smart :-) choice of the direction of axis z , the Hamiltonian matrix is already diagonal:

³³ See, e.g., EM Eq. (5.100). As a reminder, we have already used this expression for the derivation of Eq. (3).

³⁴ See, e.g., CM Sec. 6.5, in particular Eq. (6.72), and EM Sec. 5.5, in particular Eq. (5.114) and its discussion.

$$H = -\frac{\hbar\Omega}{2}\sigma_z = \frac{\hbar\Omega}{2}\begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix}, \quad (4.166)$$

meaning that $\uparrow$ and $\downarrow$ are the eigenstates of the system, with eigenenergies, respectively,

$$E_{\uparrow} = -\frac{\hbar\Omega}{2} \quad \text{and} \quad E_{\downarrow} = +\frac{\hbar\Omega}{2}. \quad (4.167)$$

Spin-1/2 in
magnetic
field:
eigen-
energies

(Note that their difference,

$$\Delta E \equiv |E_{\uparrow} - E_{\downarrow}| = \hbar|\Omega| = \hbar|\gamma\mathcal{B}|, \quad (4.168)$$

corresponds to the classical energy $2|m\mathcal{B}|$ of flipping the magnetic dipole with moment $m = \gamma\hbar/2$, oriented along the direction of field $\mathcal{B}$.³⁵) With that, Eq. (161) immediately yields following expressions for the time evolution of the expansion coefficients:

$$\alpha_{\uparrow}(t) = \alpha_{\uparrow}(t_0) \exp\left\{\frac{i}{2}\Omega(t-t_0)\right\}, \quad \alpha_{\downarrow}(t) = \alpha_{\downarrow}(t_0) \exp\left\{-\frac{i}{2}\Omega(t-t_0)\right\}, \quad (4.169)$$

allowing a ready calculation of time evolution of the expectation values of any observable.

In particular, we can calculate the expectation value of S_z as a function of time by applying Eq. (130) to an arbitrary time moment t :

$$\langle S_z \rangle(t) = \frac{\hbar}{2} [\alpha_{\uparrow}(t)\alpha_{\uparrow}^*(t) - \alpha_{\downarrow}(t)\alpha_{\downarrow}^*(t)] = \frac{\hbar}{2} [\alpha_{\uparrow}(0)\alpha_{\uparrow}^*(0) - \alpha_{\downarrow}(0)\alpha_{\downarrow}^*(0)] = \langle S_z \rangle(0). \quad (4.170)$$

Thus the expectation value of the spin component parallel to the applied magnetic field remains constant, regardless of the initial state of the system. However, this is not true for the components perpendicular to the field. For example, Eq. (132), applied to moment t , gives

$$\langle S_x \rangle(t) = \frac{\hbar}{2} [\alpha_{\uparrow}(t)\alpha_{\downarrow}^*(t) + \alpha_{\downarrow}(t)\alpha_{\uparrow}^*(t)] = \frac{\hbar}{2} [\alpha_{\uparrow}(0)\alpha_{\downarrow}^*(0)e^{i\Omega(t-t_0)} + \alpha_{\downarrow}(0)\alpha_{\uparrow}^*(0)e^{-i\Omega(t-t_0)}]. \quad (4.171)$$

Clearly, this expression describes sinusoidal oscillations with frequency (165). The amplitude and phase of these oscillations depend on initial conditions. Indeed, solving Eqs. (132)-(133) for the expansion coefficient products, we get relations

$$\hbar\alpha_{\downarrow}(t)\alpha_{\uparrow}^*(t) = \langle S_x \rangle(t) - i\langle S_y \rangle(t), \quad \hbar\alpha_{\uparrow}(t)\alpha_{\downarrow}^*(t) = \langle S_x \rangle(t) + i\langle S_y \rangle(t) \quad (4.172)$$

valid for any time t . Plugging their values for $t = 0$ into Eq. (171), we get

$$\begin{aligned} \langle S_x \rangle(t) &= \frac{1}{2} [\langle S_x \rangle(0) + i\langle S_y \rangle(0)] e^{i\Omega(t-t_0)} + \frac{1}{2} [\langle S_x \rangle(0) - i\langle S_y \rangle(0)] e^{-i\Omega(t-t_0)} \\ &\equiv \langle S_x \rangle(0) \cos \Omega t + \langle S_y \rangle(0) \sin \Omega t. \end{aligned} \quad (4.173)$$

An absolutely similar calculation using Eq. (133) gives

³⁵ Note also that if the product $\gamma\mathcal{B}$ is positive, so is Ω , so that $E_{\uparrow}$ is negative, while $E_{\downarrow}$ is positive. This is in the correspondence with the classical picture of a magnetic dipole $\mathbf{m}$ having negative potential energy when it is aligned with the external magnetic field $\mathcal{B}$ – see Eq. (162).

$$\langle S_y \rangle(t) = \langle S_y \rangle(0) \cos \Omega t - \langle S_x \rangle(0) \sin \Omega t. \quad (4.174)$$

These formulas show, for example, if at moment $t = 0$ the spin's state was $\uparrow$, i.e. $\langle S_x \rangle(0) = \langle S_y \rangle(0) = 0$, then the amplitude of oscillation of the both “lateral” component of spin vanishes. On the other hand, if the spin was initially in state $\rightarrow$, i.e. had the definite, maximum possible value of S_x , equal to $\hbar/2$ (in classics, we would say “the spin $\hbar/2$ was oriented in direction x ”), then both expectation values $\langle S_x \rangle$ and $\langle S_y \rangle$ oscillate in time³⁶ with this amplitude, with the phase shift $\pi/2$ between them. These formulas may be interpreted as the torque-induced precession of the Cartesian components of the spin vector of length $S = \hbar/2$, confined in plane $[x, y]$, with classical frequency $\Omega = \gamma \mathcal{B}$ about axis z (counterclockwise if $\gamma \mathcal{B} > 0$).

Thus, the gyromagnetic ratio is just the angular frequency of the torque-induced precession of spin (about field's direction) per unit magnetic field; for electrons, $|\gamma_e| \approx 1.761 \times 10^{11} \text{ s}^{-1} \text{ T}^{-1}$; for protons, the ratio is much smaller because of their larger mass: $\gamma_p \approx 2.675 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$, and for larger spin- $1/2$ nuclei, γ may be much smaller still – e.g., $8.681 \times 10^6 \text{ s}^{-1} \text{ T}^{-1}$ for the ^{57}Fe nucleus.³⁷

Note, however, that this classical language does not describe large quantum-mechanical uncertainties of these observables, which are absent in the classical picture of the precession – at least when it starts from a definite orientation of the angular momentum vector.

Now let us return to the discussion of the general Schrödinger equation (158) and prove the following fascinating fact: it is possible to write the general solution of this *operator* equation. In the easiest case when the Hamiltonian is time-independent, this solution is an exact analog of Eq. (161),

$$\hat{u}(t, t_0) = \hat{u}(t_0, t_0) \exp \left\{ -\frac{i}{\hbar} \hat{H}(t - t_0) \right\} = \hat{I} \exp \left\{ -\frac{i}{\hbar} \hat{H}(t - t_0) \right\}. \quad (4.175)$$

To start its proof we should, first of all, understand what does a function (in this case, the exponent) of an operator mean. In the operator (and matrix) algebra, such functions are *defined* by their Taylor expansions; in particular, Eq. (175) means that

$$\begin{aligned} \hat{u}(t, t_0) &= \hat{I} + \sum_{k=1}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar} \hat{H} t \right)^k \\ &= \hat{I} + \frac{1}{1!} \left(-\frac{i}{\hbar} \right) \hat{H} (t - t_0) + \frac{1}{2!} \left(-\frac{i}{\hbar} \right)^2 \hat{H}^2 (t - t_0)^2 + \frac{1}{3!} \left(-\frac{i}{\hbar} \right)^3 \hat{H}^3 (t - t_0)^3 + \dots, \end{aligned} \quad (4.176)$$

where $\hat{H}^2 \equiv \hat{H}\hat{H}$, $\hat{H}^3 \equiv \hat{H}\hat{H}\hat{H}$, etc. Working with such infinite series of operator products is not as hard as one could imagine, due to their regular structure. For example, let us differentiate Eq. (176) over t :

³⁶ This is one more (hopefully, redundant :-)) illustration of the difference between averaging over the statistical ensemble and over time: in Eqs. (170), (173)-(174), and quite a few relations below, only the former averaging has been performed, so the results are still functions of time.

³⁷ Such composite particles as nuclei (and, from the point of view of high-energy physics, even such hadrons as protons) may be characterized by a certain net spin (and hence by certain γ) only if during the considered process their internal degrees of freedom remain in a certain (usually, ground) quantum state.

$$\begin{aligned}\hat{u}(t, t_0) &= \hat{0} + \frac{1}{1!} \left(-\frac{i}{\hbar} \right) \hat{H} + \frac{1}{2!} \left(-\frac{i}{\hbar} \right)^2 \hat{H}^2 2(t-t_0) + \frac{1}{3!} \left(-\frac{i}{\hbar} \right)^3 \hat{H}^3 3(t-t_0)^2 + \dots \\ &= \left(-\frac{i}{\hbar} \right) \hat{H} \left[\hat{I} + \frac{1}{1!} \left(-\frac{i}{\hbar} \right) \hat{H}(t-t_0) + \frac{1}{2!} \left(-\frac{i}{\hbar} \right)^2 \hat{H}^2(t-t_0)^2 \right] + \dots = -\frac{i}{\hbar} \hat{H} \hat{u}(t, t_0),\end{aligned}\quad (4.177)$$

so that the differential equation (158) is indeed satisfied. On the other hand, Eq. (175) also satisfies the initial condition

$$\hat{u}(t_0, t_0) = \hat{u}^\dagger(t_0, t_0) = \hat{I}, \quad (4.178)$$

which immediately follows from the definition (157) of the evolution operator, so it is indeed the (unique) solution for the time evolution operator – in the Schrödinger picture.

Now let us allow operator $\hat{H}$ to be a function of time, but with the condition that its “values” (in fact, operators) at different instants commute with each other:

$$[\hat{H}(t'), \hat{H}(t'')] = 0, \quad \text{for any } t', t''. \quad (4.179)$$

(An important example of such a Hamiltonian is that of a particle under the effect of a classical, time-dependent force $\mathbf{F}(t)$):

$$\hat{H}_F = -\mathbf{F}(t) \cdot \hat{\mathbf{r}}. \quad (4.180)$$

Indeed, the radius-vector operator $\hat{\mathbf{r}}$ does not depend explicitly on time and hence commutes with itself, as well as with c -numbers $\mathbf{F}(t')$ and $\mathbf{F}(t'')$. In this case it is sufficient to replace, in all above formulas, product $\hat{H}(t-t_0)$ with the corresponding integral over time; in particular, Eq. (175) is generalized as

$$\hat{u}(t, t_0) = \hat{I} \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t') dt' \right\}. \quad (4.181)$$

Evolution operator: explicit expression

This replacement means that the first form of Eq. (176) should be replaced with

$$\hat{u}(t, t_0) = \hat{I} + \sum_{k=1}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar} \right)^k \left(\int_{t_0}^t \hat{H}(t') dt' \right)^k = \hat{I} + \sum_{k=1}^{\infty} \left(-\frac{i}{\hbar} \right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k \hat{H}(t_1) \hat{H}(t_2) \dots \hat{H}(t_k). \quad (4.182)$$

The proof that the first form of Eq. (182) satisfies Eq. (158) is absolutely similar to the one carried out above.

We may now use Eq. (181) to show that the time-evolution operator is unitary at any moment, even for the time-dependent Hamiltonian. Indeed, from that formula,

$$\hat{u}(t, t_0) \hat{u}^\dagger(t, t_0) = \hat{I} \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t') dt' \right\} \hat{I} \exp \left\{ +\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t'') dt'' \right\}. \quad (4.183)$$

Since each of the exponents may be presented with the Taylor series (182), and, thanks to Eq. (179), different components of these sums may be swapped at will, expression (183) may be manipulated exactly as the product of c -number exponents, in particular rewritten it as

$$\hat{u}(t, t_0) \hat{u}^\dagger(t, t_0) = \hat{I} \exp \left\{ -\frac{i}{\hbar} \left[\int_{t_0}^t \hat{H}(t') dt' - \int_{t_0}^t \hat{H}(t'') dt'' \right] \right\} = \hat{I} \exp \{0\} = \hat{I}. \quad (4.184)$$

This property ensures, in particular, that the system state's normalization does not depend on time:

$$\langle \alpha(t) | \alpha(t) \rangle = \langle \alpha(t_0) | \hat{u}^\dagger(t, t_0) \hat{u}(t, t_0) | \alpha(t_0) \rangle = \langle \alpha(t_0) | \alpha(t_0) \rangle. \quad (4.185)$$

The most difficult cases for the explicit solution of Eq. (158) are those when Eq. (179) is violated.³⁸ It may be proven that in these cases the integral limits in the last form of Eq. (182) should be truncated, giving the so-called *Dyson series*

$$\hat{u}(t, t_0) = \hat{I} + \sum_{k=1}^{\infty} \left(-\frac{i}{\hbar} \right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k \hat{H}(t_1) \hat{H}(t_2) \dots \hat{H}(t_k). \quad (4.186)$$

Since we would not have time to use this relation in our course, I will skip its proof.³⁹

Let me now return to the general discussion of quantum dynamics to outline its alternative, *Heisenberg picture*. For that, let us recall that according to Eq. (125), in quantum mechanics the expectation value of any observable A is a long bra-ket. Below we will see that other quantities (say, the rates of quantum transitions between pairs of different states, say α and β) may also be measured in experiment; the most general form for all such measurable quantities is the following long bracket:

$$\langle \alpha | \hat{A} | \beta \rangle. \quad (4.187)$$

As has been discussed above, in the Schrödinger picture the bra- and ket-vectors of the states are time-dependent, while the variable operators stay constant (if the corresponding variables do not explicitly depend on time), so that Eq. (187), applied to moment t , may be presented as

$$\langle \alpha(t) | \hat{A}_S | \beta(t) \rangle, \quad (4.188)$$

where index “S” emphasizes the Schrödinger picture. Let us apply to the bra- and ket-vectors in this expression the evolution law (157):

$$\langle \alpha | \hat{A} | \beta \rangle = \langle \alpha(t_0) | \hat{u}^\dagger(t, t_0) \hat{A}_S \hat{u}(t, t_0) | \beta(t_0) \rangle. \quad (4.189)$$

This equality means that if we form a long bracket with bra- and ket-vectors of the initial-time states, together with the following time-dependent *Heisenberg operator*⁴⁰

$$\hat{A}_H(t) \equiv \hat{u}^\dagger(t, t_0) \hat{A}_S \hat{u}(t, t_0) = \hat{u}^\dagger(t, t_0) \hat{A}_H(t_0) \hat{u}(t, t_0), \quad (4.190)$$

all experimentally measurable results will remain the same as in the Schrödinger picture:

$$\langle \alpha | \hat{A} | \beta \rangle = \langle \alpha(t_0) | \hat{A}_H(t, t_0) | \beta(t_0) \rangle. \quad (4.191)$$

Heisenberg
operator

Long bracket
in the
Heisenberg
picture

³⁸ We will run into such situations in Chapter 7, but will not need to apply Eq. (186).

³⁹ It may be found, for example, in Chapter 5 of J. Sakurai's textbook – see References.

⁴⁰ Note this relation is similar in structure to the symbolic Eqs. (94).

Let us see how does the Heisenberg picture work for the same simple (but very important!) problem of the spin- $\frac{1}{2}$ precession in a z -oriented magnetic field, described (in the z -basis) by the Hamiltonian matrix (164). In that basis, Eq. (158) for the time-evolution operator reads

$$i\hbar \begin{pmatrix} \dot{u}_{11} & \dot{u}_{12} \\ \dot{u}_{21} & \dot{u}_{22} \end{pmatrix} = \frac{\hbar\Omega}{2} \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix} \begin{pmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{pmatrix} = \frac{\hbar\Omega}{2} \begin{pmatrix} -u_{11} & -u_{12} \\ u_{21} & u_{22} \end{pmatrix}. \quad (4.192)$$

We see that in this simple case the equations for different matrix elements of the evolution operator matrix are decoupled, and readily solvable, using the universal initial condition (178):⁴¹

$$u(t,0) = \begin{pmatrix} e^{i\Omega t/2} & 0 \\ 0 & e^{-i\Omega t/2} \end{pmatrix} \equiv I \cos \frac{\Omega t}{2} + i\sigma_z \sin \frac{\Omega t}{2}. \quad (4.193)$$

Now we can use Eq. (190) to find the Heisenberg-picture operators of spin components. Dropping index “H” for brevity (the Heisenberg-picture operators are clearly marked by their dependence on time anyway), we get

$$\begin{aligned} S_x(t) &= u^\dagger(t,0) S_x(0) u(t,0) = \frac{\hbar}{2} u^\dagger(t,0) \sigma_x u(t,0) \\ &= \frac{\hbar}{2} \begin{pmatrix} e^{-i\Omega t/2} & 0 \\ 0 & e^{i\Omega t/2} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} e^{i\Omega t/2} & 0 \\ 0 & e^{-i\Omega t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & e^{-i\Omega t} \\ e^{i\Omega t} & 0 \end{pmatrix} = \frac{\hbar}{2} [\sigma_x \cos \Omega t + \sigma_y \sin \Omega t] \equiv S_x(0) \cos \Omega t + S_y(0) \sin \Omega t. \end{aligned} \quad (4.194)$$

Absolutely similar calculations of the other spin components yield

$$S_y(t) = \frac{\hbar}{2} \begin{pmatrix} 0 & -ie^{-i\Omega t} \\ ie^{i\Omega t} & 0 \end{pmatrix} = \frac{\hbar}{2} [\sigma_y \cos \Omega t - \sigma_x \sin \Omega t] \equiv S_y(0) \cos \Omega t - S_x(0) \sin \Omega t, \quad (4.195)$$

$$S_z(t) = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2} \sigma_z = S_z(0). \quad (4.196)$$

A practical advantage of these formulas is that they describe system’s evolution for *arbitrary* initial conditions, thus making the analysis of the initial state effects very simple. Indeed, since in the Heisenberg picture the expectation values of observables are calculated using Eq. (191) (with $\beta = \alpha$), with time-independent bra- and ket vectors, such averaging of Eqs. (194)-(196) immediately returns us to Eqs. (170), (173), and (174), obtained in the Schrödinger picture. Moreover, these equations for the Heisenberg operators formally coincide with the classical equations of the torque-induced precession for c -number variables. (In the next chapter, we will see that the same exact mapping is valid for the Heisenberg picture of the orbital motion.)

⁴¹ We could of course use this equation result, together with Eq. (157), to obtain all the above results for this system within the Schrödinger picture. In our simple case, the use of Eqs. (161) for this purpose was more straightforward, but in some cases (e.g., for time-dependent Hamiltonians) an explicit calculation of the time-evolution matrix may be the only practicable way to proceed.

In order to see that the last fact is by no means a coincidence, let us combine Eqs. (158) and (190) to form an explicit differential equation of the Heisenberg operator evolution. For that, let us differentiate Eq. (190) over time:

$$\frac{d}{dt} \hat{A}_H = \frac{\partial \hat{u}^\dagger}{\partial t} \hat{A}_S \hat{u} + \hat{u}^\dagger \frac{\partial \hat{A}_S}{\partial t} \hat{u} + \hat{u}^\dagger \hat{A}_S \frac{\partial \hat{u}}{\partial t}. \quad (4.197)$$

Plugging in the derivatives of the time evolution operator from Eq. (158) and its Hermitian conjugate, and multiplying both parts of the equation by $i\hbar$, we get

$$i\hbar \frac{d}{dt} \hat{A}_H = -\hat{u}^\dagger \hat{H} \hat{A}_S \hat{u} + \hat{u}^\dagger \frac{\partial \hat{A}_S}{\partial t} \hat{u} + \hat{u}^\dagger \hat{A}_S \hat{H} \hat{u}. \quad (4.198a)$$

If for the Schrödinger-picture Hamiltonian the condition similar to Eq. (179) is satisfied, then, according to Eqs. (177) or (182), the Hamiltonian commutes with the time evolution operator and its Hermitian conjugate, and may be swapped with any of them.⁴² Hence, we may rewrite Eq. (198a) as

$$i\hbar \frac{d}{dt} \hat{A}_H = -\hat{H} \hat{u}^\dagger \hat{A}_S \hat{u} + i\hbar \hat{u}^\dagger \frac{\partial \hat{A}_S}{\partial t} \hat{u} + \hat{u}^\dagger \hat{A}_S \hat{H} \hat{u} = i\hbar \hat{u}^\dagger \frac{\partial \hat{A}_S}{\partial t} \hat{u} + [\hat{u}^\dagger \hat{A}_S \hat{u}, \hat{H}]. \quad (4.198b)$$

Now using the definition (190) again, for both terms in the right-hand part, we may write

Heisenberg
equation
of motion

$$i\hbar \frac{d}{dt} \hat{A}_H = i\hbar \left(\frac{\partial \hat{A}}{\partial t} \right)_H + [\hat{A}_H, \hat{H}]. \quad (4.199)$$

This is the so-called *Heisenberg equation of motion*.⁴³

Let us see how does this equation look for the same problem of spin- $\frac{1}{2}$ precession in a z -oriented, time-independent magnetic field, described in the z -basis by the Hamiltonian matrix (164), which does not depend on time. In this basis, Eq. (199) for the vector operator of spin reads⁴⁴

$$i\hbar \begin{pmatrix} \dot{\mathbf{S}}_{11} & \dot{\mathbf{S}}_{12} \\ \dot{\mathbf{S}}_{21} & \dot{\mathbf{S}}_{22} \end{pmatrix} = \frac{\hbar\Omega}{2} \left[\begin{pmatrix} \mathbf{S}_{11} & \mathbf{S}_{12} \\ \mathbf{S}_{21} & \mathbf{S}_{22} \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix} \right] = \hbar\Omega \begin{pmatrix} 0 & \mathbf{S}_{12} \\ -\mathbf{S}_{21} & 0 \end{pmatrix}. \quad (4.200)$$

Once again, the equations for different matrix elements are decoupled, and their solution is elementary:

$$\begin{aligned} \mathbf{S}_{11}(t) &= \mathbf{S}_{11}(0) = \text{const}, & \mathbf{S}_{22}(t) &= \mathbf{S}_{22}(0) = \text{const}, \\ \mathbf{S}_{12}(t) &= \mathbf{S}_{12}(0)e^{i\Omega t}, & \mathbf{S}_{21}(t) &= \mathbf{S}_{21}(0)e^{-i\Omega t}. \end{aligned} \quad (4.201)$$

⁴² Due to the same reason, $\hat{H}_H \equiv \hat{u}^\dagger \hat{H}_S \hat{u} = \hat{u}^\dagger \hat{u} \hat{H}_S = \hat{H}_S$; this is why the index of the Hamiltonian operator may be dropped in Eqs. (198)-(199).

⁴³ Reportedly, this equation was derived by P. A. M. Dirac, who was so generous that he himself gave the name of his colleague to this key result, because “Heisenberg was saying something like this”.

⁴⁴ Using commutation relations (155), this equation may be readily generalized to the case of arbitrary magnetic field $\mathcal{B}(t)$ and arbitrary state basis – the exercise highly recommended to the reader.

According to Eq. (190), the initial “values” of the Heisenberg-picture matrix elements are just the Schrödinger-picture ones, so that using Eq. (117) we may rewrite this solution in either of two forms:

$$\begin{aligned} \mathbf{S}(t) &= \frac{\hbar}{2} \left[\mathbf{n}_x \begin{pmatrix} 0 & e^{-i\Omega t} \\ e^{i\Omega t} & 0 \end{pmatrix} + \mathbf{n}_y \begin{pmatrix} 0 & -ie^{-i\Omega t} \\ ie^{i\Omega t} & 0 \end{pmatrix} + \mathbf{n}_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \\ &= \frac{\hbar}{2} \begin{pmatrix} \mathbf{n}_z & \mathbf{n}_- e^{-i\Omega t} \\ \mathbf{n}_+ e^{i\Omega t} & -\mathbf{n}_z \end{pmatrix}, \quad \text{with } \mathbf{n}_{\pm} \equiv \mathbf{n}_x \pm i\mathbf{n}_y. \end{aligned} \quad (4.202)$$

The simplicity of the last expression is spectacular. (Remember, it covers *any* initial conditions, and *all* 3 spatial components of spin!) On the other hand, for some purposes the former expression may be more convenient; in particular, its Cartesian components immediately give our earlier results (194)-(196).

One of advantages is that the Heisenberg picture is that it provides a more clear link between the classical and quantum mechanics. Indeed, analytical classical mechanics may be used to derive the following equation of time evolution of an arbitrary function $A(q_j, p_j, t)$ of generalized coordinates and momenta of the system, and time:⁴⁵

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} - \{A, H\}, \quad (4.203)$$

where H is the classical *Hamiltonian function* of the system, and $\{...,...\}$ is the so-called *Poisson bracket* defined, for two arbitrary functions $A(q_j, p_j, t)$ and $B(q_j, p_j, t)$, as

$$\{A, B\} \equiv \sum_j \left(\frac{\partial A}{\partial p_j} \frac{\partial B}{\partial q_j} - \frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} \right). \quad (4.204) \quad \text{Poisson bracket}$$

Comparing Eq. (203) with Eq. (199), we see that the correspondence between the classical and quantum mechanics (in the Heisenberg picture) is provided by the following symbolic relation⁴⁶

$$\{A, B\} \leftrightarrow \frac{i}{\hbar} [\hat{A}, \hat{B}]. \quad (4.205) \quad \text{Classical vs. quantum mechanics}$$

⁴⁵ See, e.g., CM Eq. (10.17). Also, please excuse my use, for the Poisson bracket, the same (traditional) symbol $\{...,...\}$ as for the anticommutator. We will not run into the Poisson brackets again in the course, leaving very little chance for confusion.

⁴⁶ Since we have run into the commutator of Heisenberg-picture operators, let me note emphasize again that the “values” of such an operator at different moments of time often do not commute. Perhaps the simplest example is the operator $\hat{x}$ of coordinate of a free 1D particle, with Hamiltonian $\hat{H} = \hat{p}^2 / 2m$. Indeed, in this case Eq. (199) yields equations $i\hbar \dot{\hat{x}} = [\hat{x}, \hat{H}] = i\hbar \hat{p} / m$ and $i\hbar \dot{\hat{p}} = [\hat{p}, \hat{H}] = 0$, with simple solutions (similar to those for classical motion of the corresponding observables): $\hat{p}(t) = \text{const} = \hat{p}(0)$, $\hat{x}(t) = \hat{x}(0) + \hat{p}(0)t / m$, so that $[\hat{x}(0), \hat{x}(t)] = [\hat{x}(0), \hat{p}(0)]t / m = [\hat{x}_s, \hat{p}_s]t / m = i\hbar t / m \neq 0$, if $t \neq 0$.

This relation may be used, in particular, for finding appropriate operators for system's observables, if their form is not immediately evident from the correspondence principle. We will develop this argumentation further in the next chapter where we revisit the wave mechanics, and also in Chapter 9.

Finally, let us discuss one more alternative picture of quantum dynamics. It is also attributed to P. A. M. Dirac, and is called either the “Dirac picture”, or (more frequently) the *interaction picture*. The last name stems from the fact that this picture is very useful for the *perturbative* (approximate) approaches to systems whose Hamiltonians may be partitioned into two parts,

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (4.206)$$

where $\hat{H}_0$ is the sum of relatively simple Hamiltonians of non-interacting component sub-systems, while their second term in Eq. (206) represents their weak interaction. (Note, however, that the relations in the balance of this section are exact and not based on these assumptions.) In this case, it is natural to consider, together with the genuine unitary operator $\hat{u}(t, t_0)$ of the time evolution of the system, which obeys Eq. (158), a similarly defined unitary operator of evolution of the “unperturbed system” described by Hamiltonian $\hat{H}_0$ alone:

$$i\hbar \dot{\hat{u}}_0 = \hat{H}_0 \hat{u}_0, \quad (4.207)$$

and also the following *interaction evolution operator*,

$$\hat{u}_I \equiv \hat{u}_0^\dagger \hat{u}. \quad (4.208)$$

The sense of this definition becomes more clear if we insert the reciprocal relation,

$$\hat{u} \equiv \hat{u}_0 \hat{u}_I^\dagger \hat{u} = \hat{u}_0 \hat{u}_I, \quad (4.209)$$

and its Hermitian conjugate,

$$\hat{u}^\dagger = (\hat{u}_0 \hat{u}_I)^\dagger = \hat{u}_I^\dagger \hat{u}_0^\dagger, \quad (4.210)$$

into the basic Eq. (190) – which is valid in any picture:

$$\langle \alpha | \hat{A} | \beta \rangle = \langle \alpha(t_0) | \hat{u}^\dagger(t, t_0) \hat{A}_S \hat{u}(t, t_0) | \beta(t_0) \rangle = \langle \alpha(t_0) | \hat{u}_I^\dagger(t, t_0) \hat{u}_0^\dagger(t, t_0) \hat{A}_S \hat{u}_0(t, t_0) \hat{u}_I(t, t_0) | \beta(t_0) \rangle. \quad (4.211)$$

This relation shows that all calculations of the observable expectation values and transition rates (i.e. all the results of quantum mechanics that may be experimentally verified) are expressed by the following formula, with the standard bra-ket structure (187),

$$\langle \alpha | \hat{A} | \beta \rangle = \langle \alpha_I(t) | \hat{A}_I(t) | \beta_I(t) \rangle, \quad (4.212)$$

if we assume that *both* the state vectors *and* operators evolve in time, with the vectors evolving due to the interaction operator $\hat{u}_I$,

$$|\alpha_I(t)\rangle \equiv \langle \alpha(t_0) | \hat{u}_I^\dagger(t, t_0), \quad |\beta_I(t)\rangle \equiv \hat{u}_I(t, t_0) |\beta(t_0)\rangle, \quad (4.213)$$

while the operators' evolution being governed by the unperturbed operator $\hat{u}_0$:

$$\hat{A}_I(t) \equiv \hat{u}_0^\dagger(t, t_0) \hat{A}_S \hat{u}_0(t, t_0). \quad (4.214)$$

Interaction
evolution
operator

Interaction
picture:
state vectors

Interaction
picture:
operators

These relations describe the interaction picture of quantum dynamics. Let me defer an example of its convenience until the perturbative analysis of open quantum systems in Sec. 7.6, and here end the discussion with a proof that the interaction evolution operator satisfies the Schrödinger equation,

$$i\hbar\dot{\hat{U}}_I = \hat{H}_I \hat{U}_I, \quad (4.215)$$

in which $\hat{H}_I$ is the interaction Hamiltonian transformed in accordance with rule (214):

$$\hat{H}_I(t) \equiv \hat{U}_0^\dagger(t, t_0) \hat{H}_{\text{int}} \hat{U}_0(t, t_0). \quad (4.216)$$

The proof is very straightforward: first using definition (208), and then Eqs. (158) and the Hermitian conjugate of Eq. (207), we may write

$$\begin{aligned} i\hbar\dot{\hat{U}}_I &= i\hbar \frac{d}{dt} (\hat{U}_0^\dagger \hat{U}) = i\hbar (\dot{\hat{U}}_0^\dagger \hat{U} + \hat{U}_0^\dagger \dot{\hat{U}}) = -\hat{H}_0 \hat{U}_0^\dagger \hat{U} + \hat{U}_0^\dagger \hat{H} \hat{U} = -\hat{H}_0 \hat{U}_0^\dagger \hat{U} + \hat{U}_0^\dagger (\hat{H}_0 + \hat{H}_{\text{int}}) \hat{U} \\ &= -\hat{H}_0 \hat{U}_0^\dagger \hat{U} + \hat{U}_0^\dagger \hat{H}_0 \hat{U} + \hat{U}_0^\dagger \hat{H}_{\text{int}} \hat{U} = \left(-\hat{H}_0 \hat{U}_0^\dagger + \hat{U}_0^\dagger \hat{H}_0 \right) \hat{U} + \hat{U}_0^\dagger \hat{H}_{\text{int}} \hat{U}. \end{aligned} \quad (4.217)$$

Since $\hat{U}_0^\dagger$ may be presented as an integral of $\hat{H}_0$ (similar to Eq. (181) relating $\hat{U}$ and $\hat{H}$), these operators commute, so that the parentheses in the last form of Eq. (217) vanish. Now plugging $\hat{U}$ from Eq. (209), we get the equation,

$$i\hbar\dot{\hat{U}}_I = \hat{U}_0^\dagger \hat{H}_{\text{int}} \hat{U}_0 \hat{U}_I = \left(\hat{U}_0^\dagger \hat{H}_{\text{int}} \hat{U}_0 \right) \hat{U}_I, \quad (4.218)$$

that is equivalent to the combination of Eqs. (215) and (216).

Equation (215) shows that if the energy scale of interaction H_{int} is much weaker than the background energy H_0 , operators $\hat{U}_I$ and $\hat{U}_I^\dagger$, and hence the state vectors (213) evolve relatively slowly. Such an exclusion of fast background oscillations is especially convenient for the perturbative approaches to complex interacting systems, in particular to the open quantum systems that weakly interact with their environment – see Sec. 7.6.

4.7. Exercise problems

4.1. Let α and β be two possible quantum states of the same system, and $\hat{A}$ be a linear operator. Which of the following expressions are legitimate (i. e. have a well-defined meaning) within the bra-ket formalism?

- | | | | | |
|-------------------------------|---------------------------------------|----------------------------------|----------------|--------------------------------|
| 1. $\langle \alpha \rangle$ | 2. $\langle \alpha \beta \rangle^2$ | 3. $ \alpha\rangle\langle\beta $ | 4. $\hat{A}^*$ | 5. $\langle \hat{A} $ |
| 6. $\langle \alpha \hat{A}$ | 7. $\alpha \hat{A} \rangle$ | 8. $ \alpha\rangle^2$ | 9. $\hat{A}^2$ | 10. $\langle \alpha ^\dagger$ |

4.2. Prove that if $\hat{A}$ and $\hat{B}$ are linear operators, then:

- (i) $(\hat{A}^\dagger)^\dagger = \hat{A}$; (ii) $(i\hat{A})^\dagger = -i\hat{A}^\dagger$; (iii) $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$;
 (iv) operators $\hat{A}\hat{A}^\dagger$ and $\hat{A}^\dagger \hat{A}$ are Hermitian.

4.3. Prove that for any linear operators $\hat{A}, \hat{B}, \hat{C}, \hat{D}$,

$$[\hat{A}\hat{B}, \hat{C}\hat{D}] = \hat{A}\{\hat{B}, \hat{C}\}\hat{D} - \hat{A}\hat{C}\{\hat{B}, \hat{D}\} + \{\hat{A}, \hat{C}\}\hat{D}\hat{B} - \hat{C}\{\hat{A}, \hat{D}\}\hat{B}.$$

4.4. Calculate all possible binary products $\sigma_j \sigma_{j'}$ (for $j, j' = x, y, z$) of the Pauli matrices (105),

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

and their commutators and anticommutators (defined similarly to those of the corresponding operators). Present the results using the Kronecker delta and Levi-Civita permutation symbols.⁴⁷

4.5. Calculate the following expressions,

(i) $(\mathbf{c} \cdot \boldsymbol{\sigma})^n$, and then

(ii) $(bI + \mathbf{c} \cdot \boldsymbol{\sigma})^n$,

for the scalar product $\mathbf{c} \cdot \boldsymbol{\sigma}$ of the Pauli matrix vector $\boldsymbol{\sigma} \equiv \mathbf{n}_x \sigma_x + \mathbf{n}_y \sigma_y + \mathbf{n}_z \sigma_z$ by an arbitrary c -number vector $\mathbf{c}$, where $n \geq 0$ is an integer, and b is an arbitrary scalar c -number.

Hint: For task (ii), you may like to use the binomial theorem,⁴⁸ and then transform the result in a way enabling you to use the same theorem backwards.

4.6.* Use the results of the previous problem to derive Eqs. (2.165)-(2.166) for the transparency T of a system of N similar, equidistant, delta-functional tunnel barriers.

4.7. Use result of Problem 5 to spell out the following the following matrix: $\exp\{i\theta \mathbf{n} \cdot \boldsymbol{\sigma}\}$, where $\boldsymbol{\sigma}$ is the vector of Pauli matrices, $\mathbf{n}$ is a c -number vector of unit length, and θ is a c -number scalar.

4.8. Use the result of Problem 5(ii) to calculate $\exp\{A\}$, where A is an arbitrary 2×2 matrix.

4.9. Express elements of matrix $B = \exp\{A\}$ explicitly via those of the 2×2 matrix A . Spell out your result for the following matrices:

$$A = \begin{pmatrix} a & a \\ a & a \end{pmatrix}, \quad A' = \begin{pmatrix} i\varphi & i\varphi \\ i\varphi & i\varphi \end{pmatrix},$$

with real a and φ .

4.10. Prove that for arbitrary square matrices A and B ,

$$\text{Tr}(AB) = \text{Tr}(BA).$$

Is each diagonal element $(AB)_{jj}$ necessarily equal to $(BA)_{jj}$?

⁴⁷ See, e.g., MA Eqs. (13.1) and (13.2).

⁴⁸ See, e.g. MA Eq. (2.9).

4.11. Prove that the matrix trace of an arbitrary operator does not change at an arbitrary unitary transformation.

4.12. Prove that for any two full and orthonormal bases u_j, v_j of the same Hilbert space,

$$\text{Tr}(|u_j\rangle\langle v_{j'}|) = \langle v_{j'} | u_j \rangle.$$

4.13. Is the 1D scattering matrix S , defined by Eq. (133), unitary? What about the 1D transfer matrix T defined by Eq. (134)?

4.14. Calculate the trace of the following matrix:

$$\exp\{i\mathbf{a} \cdot \boldsymbol{\sigma}\} \exp\{i\mathbf{b} \cdot \boldsymbol{\sigma}\},$$

where $\boldsymbol{\sigma}$ is the Pauli matrix vector, while $\mathbf{a}$ and $\mathbf{b}$ are usual (c -number) geometric vectors.

4.15. Let A_j be eigenvalues of some operator $\hat{A}$. Express the following two sums,

$$\Sigma_1 = \sum_j A_j, \quad \Sigma_2 = \sum_j A_j^2,$$

via the matrix elements $A_{jj'}$ of this operator in an arbitrary basis.

4.16. Calculate $\langle \sigma_z \rangle$ of a two-level system in a quantum state with the following ket-vector:

$$|\alpha\rangle = \text{const} \times (|\uparrow\rangle + |\downarrow\rangle + |\rightarrow\rangle + |\leftarrow\rangle),$$

where $(\uparrow, \downarrow)$ and $(\rightarrow, \leftarrow)$ are eigenstates of the Pauli matrices σ_z and σ_x , respectively.

Hint: Double-check whether the solution you are giving is general.

4.17. An electron is fully polarized in the positive z -direction. Calculate the probabilities of the alternative outcomes of a perfect Stern-Gerlach experiment with the magnetic field $\mathbf{B}$ oriented in the direction of some axis $\mathbf{n}$, performed on this electron.

4.18. A perfect Stern-Gerlach instrument makes a single-shot measurement of the following combination, $(S_x + S_z)/\sqrt{2}$, of two spin components of a z -polarized electron; after that, component S_z of the same particle is measured. What are the possible outcomes of these measurements and their probabilities?

4.19. In a certain basis, the Hamiltonian of a spin- $1/2$ (two-level) system is described by matrix

$$H = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \quad \text{with } E_1 \neq E_2,$$

and the operator of some observable A , by matrix

$$A = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

For the system's state with the energy equal exactly to E_1 , find the possible results of measurements of observable A and the probabilities of the corresponding measurement outcomes.

4.20.* States $u_{1,2,3}$ form an orthonormal basis of a system with Hamiltonian

$$\hat{H} = -\delta(|u_1\rangle\langle u_2| + |u_2\rangle\langle u_3| + |u_3\rangle\langle u_1|) + \text{h.c.},$$

where δ is a real constant, and h.c. means the Hermitian conjugate of the previous expression. Calculate its stationary states and energy levels. Can you relate this system with any other(s) discussed earlier in the course?

4.21. Suggest a Hamiltonian describing particle's dynamics in an infinite 1D set of similar quantum wells in the tight-binding approximation, in the bra-ket formalism, and verify that it yields the correct dispersion relation (2.206).

4.22. Calculate eigenvectors and eigenvalues of the following matrices:

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad B = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}.$$

4.23. Find eigenvalues of the following matrix:

$$A = \mathbf{a} \cdot \boldsymbol{\sigma} \equiv a_x \sigma_x + a_y \sigma_y + a_z \sigma_z,$$

where $a_{x,y,z}$ are real c -numbers (scalars), and $\sigma_{x,y,z}$ are the Pauli matrices. Sketch the dependence of the eigenvalues on parameter a_z , with a_x and a_y fixed. Compare the result with Fig. 29.

4.24. Derive a differential equation for the time evolution of the expectation value of an observable, using both the Schrödinger picture and the Heisenberg picture of quantum mechanics.

4.25. At $t = 0$, a spin- $1/2$ particle, whose interaction with an external field is described by Hamiltonian

$$\hat{H} = \mathbf{a} \cdot \hat{\boldsymbol{\sigma}} \equiv a_x \hat{\sigma}_x + a_y \hat{\sigma}_y + a_z \hat{\sigma}_z,$$

(where $a_{x,y,z}$ are real and constant c -numbers, and $\hat{\sigma}_{x,y,z}$ are the operators that, in the z -basis, are represented by the Pauli matrices $\sigma_{x,y,z}$), was in state $\uparrow$, one of two eigenstates of operator $\hat{\sigma}_z$. Use the Schrödinger picture equations to calculate the time evolution of:

- (i) the ket-vector $|\alpha\rangle$ of the system (in any stationary basis you like),
- (ii) the probabilities to find the system in states $\uparrow$ and $\downarrow$, and
- (iii) the expectation values of all 3 spatial components ($\hat{S}_x$, etc.) of the spin vector operator $\hat{\mathbf{S}} = (\hbar/2)\hat{\boldsymbol{\sigma}}$.

Analyze and interpret the results for the particular case $a_y = a_z = 0$.

4.26. For the same system as in the previous problem, use the Heisenberg picture equations to calculate the time evolution of:

- (i) all three spatial components ($\hat{S}_x$, etc.) of the spin operator $\hat{\mathbf{S}}_H(t)$,
- (ii) the expectation values of the spin components.

Compare the latter results with those of the previous problem.

4.27. For the same system as in two last problems, calculate the matrix elements of operator $\hat{\sigma}_z$ in the basis of eigenstates a_1, a_2 .

Hint: In contrast to the cited problems, the answer evidently does not depend on the initial conditions.

4.28. In the Schrödinger picture of quantum mechanics, three operators satisfy the following commutation relation:

$$[\hat{A}, \hat{B}] = \hat{C}.$$

What is their relation in the Heisenberg picture (at the same time instant)?

4.29. A spin- $1/2$ particle is placed into a magnetic field $\mathcal{B}(t)$, which is an arbitrary function of time. Derive the differential equations describing the time evolution of:

- (i) the vector operator $\hat{\mathbf{S}}$ of particle's spin (in the Heisenberg picture), and
- (ii) the expectation value $\langle \mathbf{S} \rangle$ of spin's vector.

Contemplate the relative merits of the latter equation for the description of a single spin and of a large collection of similar, non-interacting spins.

4.30.* Prove the Bloch theorem given by either Eq. (3.107) or Eq. (3.108).

Hint: Consider the *translation operator* $\hat{\tau}_{\mathbf{R}}$, defined by the following result of its action on an arbitrary function $f(\mathbf{r})$:

$$\hat{\tau}_{\mathbf{R}} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}),$$

where $\mathbf{R}$ is an arbitrary vector of the Bravais lattice (3.106). In particular, analyze the commutation properties of the operator, and apply them to an eigenfunction $\psi(\mathbf{r})$ of the stationary Schrödinger equation for a particle in a 3D periodic potential described by Eq. (3.105).

Chapter 5. Some Exactly Solvable Problems

This describes several simplest but important applications of the bra-ket formalism, notably including a few wave-mechanics problems we have already started to discuss in Chapters 2 and 3.

5.1. Two-level systems

In the course of discussion of the bra-ket formalism in the last chapter, we have already considered several examples of how it works for electron's spin. We have seen, in particular, that in magnetic field the electron has eigenenergies (4.167), i.e. *two energy levels*. As will be shown later in the course, such two-energy-level picture is valid not only for electrons and other spin- $\frac{1}{2}$ elementary particles (such as muons and neutrinos), but also may give a good approximation for other important quantum systems. For example, as was already mentioned in Chapter 2, two energy levels are sufficient for an approximate description of dynamics of two weakly coupled quantum wells (Sec. 2.6), and of level anticrossing in the weak-potential approximation of the band theory (Sec. 2.7). Such *two-level systems* (alternatively called “spin- $\frac{1}{2}$ -like” systems) are nowadays the focus of additional attention in the view of prospects of their possible use for information processing and encryption. (In the last context, to be discussed in Sec. 8.5, a two-level system is usually called a *qubit*.)

This is why before proceeding to other problems, let us summarize in brief what we have already learned about properties and dynamics of two-level systems, in a more convenient language. According to the general Eq. (4.6), a ket- (or bra-) vector of an arbitrary pure (coherent) state α of such a system may be presented, at any instant, as a linear combination of two basis vectors, for example

$$|\alpha\rangle = \alpha_{\uparrow}|\uparrow\rangle + \alpha_{\downarrow}|\downarrow\rangle, \quad (5.1)$$

and hence is completely described by two complex coefficients (*c*-numbers) – say, $\alpha_{\uparrow}$ and $\alpha_{\downarrow}$. These two numbers are not completely arbitrary; they are restricted by the normalization condition. If the basis vectors are normalized, then to have the system in *some* basis state with a 100% probability, we need

$$W_{\Sigma} = \langle\alpha|\alpha\rangle = (\langle\uparrow|\alpha_{\uparrow}^* + \langle\downarrow|\alpha_{\downarrow}^*)(\alpha_{\uparrow}|\uparrow\rangle + \alpha_{\downarrow}|\downarrow\rangle) = \alpha_{\uparrow}^*\alpha_{\uparrow} + \alpha_{\downarrow}^*\alpha_{\downarrow} = |\alpha_{\uparrow}|^2 + |\alpha_{\downarrow}|^2 = 1. \quad (5.2)$$

This requirement is automatically satisfied if we take the moduli of $\alpha_{\uparrow}$ and $\alpha_{\downarrow}$ equal to the sine and cosine of the same (real) angle. Thus we can write, for example,

$$\alpha_{\uparrow} = \cos\frac{\theta}{2}e^{i\gamma}, \quad \alpha_{\downarrow} = \sin\frac{\theta}{2}e^{i(\gamma+\varphi)}. \quad (5.3)$$

Moreover, according to the general Eq. (4.125), if we deal with just one system,¹ the common phase factor $\exp\{i\gamma\}$ is unimportant for calculation of any expectation values, and we can take $\gamma = 0$, so that Eq. (3) is reduced to

¹ To recall why this condition is crucial, please revisit the beginning of Sec. 2.3. Note also that, in particular, the mutual phase shifts between different qubits are very important for quantum information processing (see Chapter 7 below), so that most discussions of these applications have to start from Eq. (3) rather than Eq. (4).

$$\alpha_{\uparrow} = \cos \frac{\theta}{2}, \quad \alpha_{\downarrow} = \sin \frac{\theta}{2} e^{i\varphi}. \quad (5.4)$$

Bloch
sphere
representation
of state

The reason why the argument of sine and cosine functions is usually taken in the form $\theta/2$, becomes clear from Fig. 1a: Eq. (4) conveniently maps each state α on a certain *representation point* of a unit-radius *Bloch sphere*,² with polar angle θ and azimuthal angle φ . In particular, state $\uparrow$ (with $\alpha_{\uparrow} = 1$ and $\alpha_{\downarrow} = 0$) corresponds to the North Pole of the sphere ($\theta = 0$), while state $\downarrow$ (with $\alpha_{\uparrow} = 0$ and $\alpha_{\downarrow} = 1$), to its South pole ($\theta = \pi$).³ Similarly, states $\rightarrow$ and $\leftarrow$, described by Eqs. (4.122), i.e. having $\alpha_{\uparrow} = 1/\sqrt{2}$ and $\alpha_{\downarrow} = \pm 1/\sqrt{2}$, correspond to points with $\theta = \pi/2$ and to, respectively, $\varphi = 0$ and $\varphi = \pi$. Two more special points (denoted in Fig. 1a as $\odot$ and $\otimes$) are also located on sphere's equator (at $\theta = \pi/2$ and $\varphi = \pm \pi/2$); it is easy to check that they correspond to the eigenstates of matrix σ_y (in the same z -basis).

In order to understand why such mutually perpendicular location of these three special point pairs on the Bloch sphere is not occasional, let us plug Eqs. (4) into Eqs. (4.131)-(4.133) for the expectation values of spin components. The result is

$$\langle S_x \rangle = \frac{\hbar}{2} \sin \theta \cos \varphi, \quad \langle S_y \rangle = \frac{\hbar}{2} \sin \theta \sin \varphi, \quad \langle S_z \rangle = \frac{\hbar}{2} \cos \theta, \quad (5.5)$$

showing that the radius-vector of the representation point on the sphere is (after multiplication by $\hbar/2$) just the expectation value of the spin vector $\mathbf{S}$.

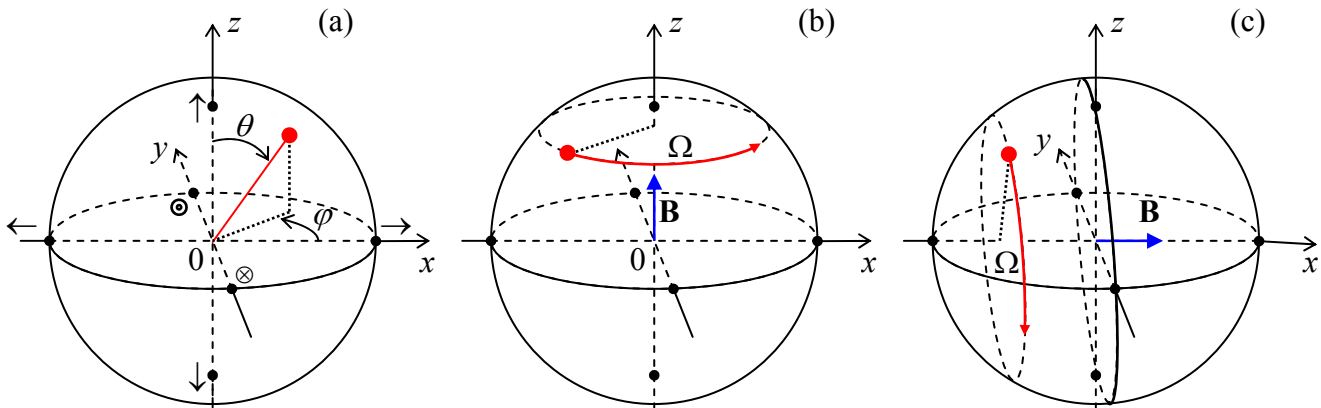


Fig. 5.1. Bloch sphere: (a) notation, and presentation of spin precession in magnetic fields directed along: (b) axis z , and (c) axis x .

Now let us see how does the representation point moves in various cases. First of all, according to Eqs. (4.157)-(4.158), in the absence of an external field (when the Hamiltonian operator is equal to zero and hence the time-evolution operator is constant) the point does not move at all. Now, if we apply to an electron a magnetic field directed along axis z , then, according to Eqs. (4.202), the Heisenberg operator of S_z (and hence the expectation value $\langle S_z \rangle$) remains constant, while angle φ in Eq. (5) evolves

² Named after the same F. Bloch who has pioneered the energy band theory that was discussed in Chapters 2-3.

³ In the quantum information literature, ket-vectors $|\uparrow\rangle$ and $|\downarrow\rangle$ of these two states of a qubit are usually denoted as $|1\rangle$ ("quantum one") and $|0\rangle$ ("quantum zero").

in time as $\Omega t + \text{const.}$ This means that the torque-induced precession of the spin in a constant field $\mathcal{B} = \mathbf{n}_z \mathcal{B}$ is described by a circular rotation of the representation point about axis z (in Fig. 1b, in the horizontal plane) with the classical precession frequency Ω . This is essentially the classical picture of rotation of the angular momentum vector about the precession axis z , with both its length and the z -component conserved.⁴

It is straightforward to repeat all calculations of Sec. 4.6 for a field of a different orientation and prove the (virtually evident) result that the representation point performs a similar rotation about the field direction. (Fig. 1c shows such rotation for an x -directed field.) Finally, note that it is sufficient to turn off the field to stop the precession instantly. (Since Eq. (4.158) is the first-order differential equation, the representation point has no effective inertia.⁵) Hence changing the direction and magnitude of the external field, it is possible to move spin's representation point to any position on the Bloch sphere. (In Chapter 6 we will examine another method of manipulating the point position, that is based on external rf field and is more convenient for some two-level systems.)

In the context of quantum information, this means that in the absence of uncontrollable interaction with environment, it is possible to prepare a qubit in any pure quantum state, and then keep it unchanged. From here it is clear that a qubit is very much different from and a classical bistable system used to store single bits of information – such as the voltage state of a usual SRAM cell (a positive-feedback loop of two transistor-based inverters). As Eq. (4) shows, qubit's state is determined by two independent, continuous parameters θ and ϕ , so it may store much more information than one bit. (The difference is even more spectacular in qubit systems, to be discussed in Sec. 8.5.) However, classical bistable systems, due to their nonlinearity, are stable with respect to small perturbations, so that their operation is rather robust with respect to unintentional interaction with their environment. In contrast, qubit's state may be readily disturbed (i.e. its representation point on the Bloch sphere shifted) by even minor perturbations, and does not have an internal state stabilization mechanism.⁶ Due to this reason, qubit-based systems are rather vulnerable to environment-induced drifts, including *dephasing* and *relaxation effects*, which will be discussed in Chapter 7.

5.2. Revisiting wave mechanics

In order to use the bra-ket formalism for the description of the “orbital” motion of a particle as a whole, we have to either rewrite or even modify some of its formulas for the case of observables with continuous spectrum of eigenvalues. (One example we already know well are the momentum and kinetic energy of a free particle.) In that case, all the above expressions for states, their bra- and ket-vectors, and eigenvalues, should be stripped of discrete indices, like index j in the key equation (68) that determines eigenstates and eigenvalues of observable A . For that, Eq. (68) may be rewritten in the form

⁴ Still, it is crucial to appreciate the difference between the *expectation values* (5), i.e. *c-numbers*, and the actual observables S_x , S_y , and S_z which are described in quantum mechanics by *operators*. For example, according to Eq. (4.156), for any position on the Bloch sphere, it is impossible to have exact values of Cartesian components, as it is in the classical picture.

⁵ The same is true for the angular momentum $\mathbf{L}$ at the classical torque-induced precession – see, e.g., CM Sec.6.5 and in particular Eq. (6.71).

⁶ In this aspect as well, the information processing systems based on qubits are closer to classical analog computers rather than classical digital ones.

$$\hat{A}|a_A\rangle = A|a_A\rangle. \quad (5.6)$$

More essentially, all sums over such continuous eigenstate sets should be replaced by integrals. For example, for a full and orthonormal set of eigenstates (6), the closure relation (4.44) should be replaced with

$$\int dA |a_A\rangle\langle a_A| = \hat{I}, \quad (5.7)$$

Continuous spectrum:
closure relation

where the integral should be taken over the whole interval of possible values of observable A . Applying this relation to the ket-vector of an arbitrary state α (generally, *not* an eigenstate of operator $\hat{A}$), we get

$$|\alpha\rangle = \hat{I}|\alpha\rangle = \int dA |a_A\rangle\langle a_A|\alpha\rangle = \int dA \langle a_A|\alpha\rangle |a_A\rangle. \quad (5.8)$$

This integral replaces sum (4.37) for the representation of an arbitrary ket-vector as an expansion over eigenstates of an operator. For the particular case when $|\alpha\rangle = |a_{A'}\rangle$, this relation requires⁷

$$\langle a_A|a_{A'}\rangle = \delta(A - A'); \quad (5.9)$$

Continuous spectrum:
state ortho-normality

this formula replaces the orthonormality condition (4.38).

According to Eq. (8), in the continuous case the bra-ket $\langle a_A|\alpha\rangle$ still plays the role of the coefficient whose modulus squared determines state a_A 's probability – see the last form of Eq. (4.120). However, in the continuous spectrum case the probability to find the system exactly in a particular state is infinitesimal. Instead we should speak about the *probability density* $w(A) \propto |\langle a_A|\alpha\rangle|^2$ to find the observable within a *small interval* dA about a certain value A . The coefficient in that relation may be found by making the similar change from summation to integration (without any additional coefficients) in the normalization condition (4.121):

$$\int dA \langle \alpha|a_A\rangle\langle a_A|\alpha\rangle = 1. \quad (5.10)$$

Since the total probability of the system to be in *some* state should also equal $\int w(A)dA$, this means that

$$w(A) = \langle \alpha|a_A\rangle\langle a_A|\alpha\rangle = |\langle \alpha|a_A\rangle|^2. \quad (5.11)$$

Continuous spectrum:
probability density

Now let us see how we can calculate expectation values of continuous observables, i.e. their ensemble averages. If we speak about the same observable A whose eigenstates are used as the basis (or any compatible observable), everything is simple. Inserting Eq. (11) into the general statistical relation

$$\langle A \rangle = \int w(A) A dA, \quad (5.12)$$

which is just the evident continuous version of Eq. (1.37), we get

$$\langle A \rangle = \int \langle \alpha|a_A\rangle A \langle a_A|\alpha\rangle dA. \quad (5.13)$$

Presenting this expression as a double integral,

$$\langle A \rangle = \int dA \int dA' \langle \alpha|a_A\rangle A \delta(A - A') \langle a_{A'}|\alpha\rangle, \quad (5.14)$$

⁷ Notice that in the contrast to the discrete spectrum case, the dimensionality of the bra- and ket-vectors so normalized is different from 1.

and using the continuous-spectrum version of Eq. (4.100),

$$\langle a_A | \hat{A} | a_{A'} \rangle = A \delta(A - A'), \quad (5.15)$$

we may write

Expectation
value

$$\langle A \rangle = \int dA \int dA' \langle \alpha | a_A \rangle \langle a_A | \hat{A} | a_{A'} \rangle \langle a_{A'} | \alpha \rangle = \langle \alpha | \hat{A} | \alpha \rangle, \quad (5.16)$$

so that Eq. (4.125) remains valid in the continuous-spectrum case without any changes.

The situation is a bit more complicated for the expectation values of operators that do not commute with the base-creating operator, because the matrix of such an operators in that may not be diagonal. We will consider (and overcome :-)) this technical difficulty very soon, but otherwise we are ready for the discussion of wave mechanics. (For the notation simplicity I will discuss its 1D version; the generalization to the 2D and 3D cases is straightforward.)

Let us consider what is called the *coordinate representation*, postulating the (intuitively almost evident) existence of a quantum state basis, whose with ket-vectors will be called $|x\rangle$, corresponding to a certain, exactly defined value x of particle's coordinate. Writing the following evident identity:

$$x|x\rangle = x|x\rangle, \quad (5.17)$$

and comparing this relation with Eq. (6), we see that they do not contradict each other if we assume that x in the left-hand part of this equation is considered as the coordinate operator $\hat{x}$ whose action on a ket- (or bra-) vector is just its multiplication by c-number x . (This looks like a proof, but is actually a separate, independent postulate, no matter how plausible.)

In this coordinate representation, the inner product $\langle a_A | \alpha(t) \rangle$ becomes $\langle x | \alpha(t) \rangle$, and Eq. (11) takes the form

$$w(x, t) = \langle \alpha(t) | x \rangle \langle x | \alpha(t) \rangle = \langle x | \alpha(t) \rangle^* \langle x | \alpha(t) \rangle. \quad (5.18)$$

Comparing this formula with the basic postulate (1.22) of wave mechanics, we see that they coincide if the Schrödinger's wavefunction of time-evolving state $\alpha(t)$ is identified with that bra-ket:⁸

Wave-
function
as inner
product

$$\Psi_\alpha(x, t) = \langle x | \alpha(t) \rangle. \quad (5.19)$$

This key formula provides the connection between the bra-ket formalism and wave mechanics, and should not be too surprising for the (thoughtful :-)) reader. Indeed, Eqs. (4.45) shows that any inner product of vectors describing two states is a measure of their coincidence - just as the scalar product of two geometric vectors. (The orthonormality condition (4.38) is a particular manifestation of this fact.) In this language, value (19) of wavefunction Ψ_α at point x and moment t characterizes “how much of a particular coordinate x ” does the state α contain at that particular instance. (Of course this informal language is too crude to describe the fact that $\Psi_\alpha(x, t)$ is a complex function, which has not only a modulus, but also a phase.)

⁸ I do not quite like expressions like $\langle x | \Psi \rangle$ used in some papers and even textbooks. Of course, one is free to replace α with any other letter (Ψ including) to denote a quantum state, but then it is better not to use the same letter to denote the wavefunction, i.e. an inner product of two state vectors, to avoid confusion.

Let us rewrite the most important formulas of the bra-ket formalism (so far, in the Schrödinger picture) in the wave mechanics notation. In particular, let us use Eq. (19) to calculate the (partial) time derivative of the wavefunction, multiplied by the usual coefficient $i\hbar$:

$$i\hbar \frac{\partial \Psi_\alpha}{\partial t} = i\hbar \frac{\partial}{\partial t} \langle x | \alpha(t) \rangle. \quad (5.20)$$

Since the coordinate operator $\hat{x}$ does not depend on time explicitly, its eigenstates x are stationary, and we can swap the time derivative and the time-independent ket-vector and hence $\langle x |$. Making use of the Schrödinger-picture equations (4.157) and (4.158), and then inserting the identity operator in the continuous form (7) of the closure relation, written for the coordinate eigenstates,

$$\int dx' |x'\rangle \langle x'| = \hat{I}, \quad (5.21)$$

we may continue to develop the right-hand part of Eq. (20) as

$$\begin{aligned} \langle x | i\hbar \frac{\partial}{\partial t} | \alpha(t) \rangle &= \langle x | i\hbar \frac{\partial}{\partial t} \hat{u}(t, t_0) | \alpha(t_0) \rangle = \langle x | \hat{H} \hat{u}(t, t_0) | \alpha(t_0) \rangle = \langle x | \hat{H} | \alpha(t) \rangle \\ &= \int dx' \langle x | \hat{H} | x' \rangle \langle x' | \alpha(t) \rangle = \int dx' \langle x | \hat{H} | x' \rangle \Psi_\alpha(x', t). \end{aligned} \quad (5.22)$$

For a general Hamiltonian operator, we have to stop here, because if it does not commute with the coordinate operator, its matrix in the x -basis is not diagonal, and integral (22) cannot be worked out explicitly. However, there exists a broad set of *space-local operators*⁹ whose arguments include just one value of the spatial coordinate, for which we can move ket-vector $\langle x |$ to the right¹⁰

$$\langle x | \hat{A} | x' \rangle \Psi(x', t) = \hat{A} \Psi(x', t) \langle x | x' \rangle = \hat{A} \Psi(x, t) \delta(x - x'). \quad (5.23)$$

Space-
local
operators

where operator $\hat{A}$ in the last two forms should be understood as its coordinate representation that is *defined* by Eq. (23) - if it is valid for a particular operator. For example, consider the 1D version of operator (1.40),

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + U(\hat{x}, t), \quad (5.24)$$

which was the basis of all our discussions in Chapter 2. Its potential-energy part commutes with operator $\hat{x}$, so its matrix in the x -basis is diagonal, meaning that this part of Hamiltonian (24) is clearly local, with its coordinate representation given merely by the c -number function $U(x, t)$. The situation with the kinetic energy, which is a function of momentum operator $\hat{p}_x$, not commuting with $\hat{x}$, is less evident. Let me show that this operator is also local, and in the same shot derive (the 1D version of) Eq. (1.26), if we *postulate* the commutation relation (2.14):

$$\hat{x} \hat{p}_x - \hat{p}_x \hat{x} = i\hbar \hat{I}. \quad (5.25)$$

⁹ Of all the operators we will encounter in this course, only the statistical operator $\hat{w}$ is substantially non-local – see Sec. 7.2.

¹⁰ In the second equality, I have use Eq. (9) for variable x .

For that, let us consider the following matrix element, $\langle x|\hat{x}\hat{p}_x - \hat{p}_x\hat{x}|x'\rangle$. On one hand, we may use Eq. (25) to write

$$\langle x|\hat{x}\hat{p}_x - \hat{p}_x\hat{x}|x'\rangle = \langle x|i\hbar\hat{I}|x'\rangle = i\hbar\langle x|x'\rangle = i\hbar\delta(x-x'). \quad (5.26)$$

On the other hand, since $\hat{x}|x'\rangle = x'|x'\rangle$ and $\langle x|\hat{x} = \langle x|x$, we can write

$$\langle x|\hat{x}\hat{p}_x - \hat{p}_x\hat{x}|x'\rangle = \langle x|x\hat{p}_x - \hat{p}_xx'|x'\rangle = (x-x')\langle x|\hat{p}_x|x'\rangle. \quad (5.27)$$

Comparing Eqs. (26) and (27), we may write

$$\langle x|\hat{p}_x|x'\rangle = i\hbar \frac{\delta(x-x')}{(x-x')}. \quad (5.28a)$$

Thus $\hat{p}_x$ is a local operator. Since Eq. (28a) may be rewritten as¹¹

$$\langle x|\hat{p}_x|x'\rangle = -i\hbar \frac{\partial}{\partial x} \delta(x-x'), \quad (5.28b)$$

its comparison with Eq. (23) shows that the formula used so much in Chapter 2,

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad (5.29)$$

is indeed valid, but *only for the coordinate representation* of the momentum operator. (Later in this section we will see that in an alternative, *momentum representation*, this operator looks completely differently.)

It is straightforward to show (and virtually evident) that any operator $f(\hat{p})$ is local as well, with its coordinate representation being

$$f\left(-i\hbar \frac{\partial}{\partial x}\right). \quad (5.30)$$

In particular, this pertains to the kinetic energy operator in Eq. (24), so that Eq. (20) is reduced to the Schrödinger equation in its familiar wave-mechanics form (1.28), if by $\hat{H}$ we mean its coordinate representation:

$$\hat{H} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x}\right)^2 + U(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x,t). \quad (5.31)$$

Now let us return, as was promised, to operators that do not commute with operator $\hat{x}$, and hence do not have to share its continuous spectrum. Inner-multiplying both parts of the general Eq. (4.68) by ket-vector $\langle x|$, and inserting into the left-hand part the identity operator in form (21), we get

$$\int dx' \langle x|\hat{A}|x'\rangle \langle x'|a_j\rangle = A_j \langle x|a_j\rangle, \quad (5.32)$$

¹¹ The equivalence of the two forms of Eq. (28) may be readily proven, for example, by comparison of their effect on any differentiable function $f(x, x')$, using its Taylor expansion over argument x at point $x' = x$ – a simple but good exercise for the reader.

i.e., using the wavefunction definition (19),

$$\int dx' \langle x | \hat{A} | x' \rangle \Psi_j(x', t) = A_j \Psi_j(x, t). \quad (5.33)$$

If the operator A is space-local, i.e. satisfies Eq. (23), then this result is immediately reduced to

$$\hat{A} \Psi_j(x, t) = A_j \Psi_j(x, t), \quad (5.34)$$

Operator's
eigenstates
and
eigenvalues

(where the left-hand part implies the coordinate representation of the operator), even if the operator does not commute with operator $\hat{x}$.¹² The most important case of this coordinate-representation form of the eigenproblem (4.68) is the familiar Eq. (1.60) for eigenvalues E_n of energy. Hence, the energy spectrum of a system (that, as we know very well from the first chapters of the course, may be discrete) is nothing more than the set of eigenvalues of its Hamiltonian operator – a very important conclusion indeed.

The operator locality also simplifies the expression for its expectation value. Indeed, plugging the completeness relation in the form (21) into the general Eq. (4.125) twice (written in the first case for x and in the second case for x'), we get

$$\langle A \rangle = \int dx \int dx' \langle \alpha(t) | x \rangle \langle x | \hat{A} | x' \rangle \langle x' | \alpha(t) \rangle = \int dx \int dx' \Psi_\alpha^*(x, t) \langle x | \hat{A} | x' \rangle \Psi_\alpha(x', t). \quad (5.35)$$

Now, Eq. (23) reduces this result to just

$$\langle A \rangle = \int dx \int dx' \Psi_\alpha^*(x, t) \hat{A} \Psi_\alpha(x', t) \delta(x - x') = \int \Psi_\alpha^*(x, t) \hat{A} \Psi_\alpha(x, t) dx. \quad (5.36)$$

i.e. to Eq. (1.23), which we had to postulate in Chapter 1.

So, we have essentially derived all basic relations of wave mechanics from the bra-ket formalism, which will also allow us to get some important new results in that area. Before doing that, let us have a look at a pair of very interesting relations, together called the *Ehrenfest theorem*. In order to derive them, let us calculate the following commutator:¹³

$$[\hat{x}, \hat{p}_x^2] \equiv \hat{x} \hat{p}_x \hat{p}_x - \hat{p}_x \hat{p}_x \hat{x}. \quad (5.37)$$

Rewriting Heisenberg's commutation relation (25) as

$$\hat{x} \hat{p}_x = \hat{p}_x \hat{x} + i\hbar, \quad (5.38)$$

we can use it twice in the first term of the right-hand part of Eq. (37) to sequentially move the momentum operators to the left:

$$\hat{x} \hat{p}_x \hat{p}_x = (\hat{p}_x \hat{x} + i\hbar) \hat{p}_x = \hat{p}_x \hat{x} \hat{p}_x + i\hbar \hat{p}_x = \hat{p}_x (\hat{p}_x \hat{x} + i\hbar) + i\hbar \hat{p}_x = \hat{p}_x \hat{p}_x \hat{x} + 2i\hbar \hat{p}_x. \quad (5.39)$$

¹² In some systems of quantum mechanics postulates, the Schrödinger equation (1.28) itself is considered as a sort of eigenstate/eigenvalue problem (34) for operator $i\hbar \partial / \partial t$. Notice that such construct is very close to that of the momentum operator $-i\hbar \partial / \partial x$, and similar arguments may be given for both expressions, starting from the invariance of the quantum state of a free particle with respect to translations in time and space, respectively.

¹³ It is not important whether we speak about the Schrödinger or Heisenberg picture here. Indeed, if three operators in the former picture are related as $[\hat{A}_S, \hat{B}_S] = \hat{C}_S$, then according to Eq. (4.190), in the latter picture

$$[\hat{A}_H, \hat{B}_H] = [\hat{U}^\dagger \hat{A}_S \hat{U}, \hat{U}^\dagger \hat{B}_S \hat{U}] = \hat{U}^\dagger \hat{A}_S \hat{U} \hat{U}^\dagger \hat{B}_S \hat{U} - \hat{U}^\dagger \hat{B}_S \hat{U} \hat{U}^\dagger \hat{A}_S \hat{U} = \hat{U}^\dagger [\hat{A}_S, \hat{B}_S] \hat{U} = \hat{U}^\dagger \hat{C}_S \hat{U} = \hat{C}_H.$$

The first term of the result cancels with the second term of Eq. (37), so that the commutator is rather simple:

$$[\hat{x}, \hat{p}_x^2] = 2i\hbar\hat{p}_x. \quad (5.40)$$

Let us use this equality to calculate the Heisenberg-picture equation of motion for operator $\hat{x}$, applying the general Heisenberg equation (4.199) to the orbital motion, when the Hamiltonian has the form (31), with time-independent potential $U(x)$:¹⁴

$$\frac{d\hat{x}}{dt} = \frac{1}{i\hbar}[\hat{x}, \hat{H}] = \frac{1}{i\hbar}\left[\hat{x}, \frac{\hat{p}_x^2}{2m} + U(\hat{x})\right]. \quad (5.41)$$

The potential energy operator commutes with the coordinate operator. Thus, the right-hand part of Eq. (41) is proportional to commutator (40):

Heisenberg
equation
for
coordinate

$$\frac{d\hat{x}}{dt} = \frac{\hat{p}_x}{m}. \quad (5.42)$$

In that *operator* equality, we readily recognize the classical relation between particle's momentum and is velocity.

Now let us see what does a similar procedure give for the momentum's derivative:

$$\frac{d\hat{p}_x}{dt} = \frac{1}{i\hbar}[\hat{p}_x, \hat{H}] = \frac{1}{i\hbar}\left[\hat{p}_x, \frac{\hat{p}_x^2}{2m} + U(\hat{x})\right]. \quad (5.43)$$

The kinetic energy operator commutes with the momentum operator, and hence may be dropped from the right-hand part of this equation. In order to calculate the remaining commutator of the momentum and potential energy, let us use the fact that any smooth potential profile may be represented by its Taylor expansion:

$$U(\hat{x}) = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k U}{\partial \hat{x}^k} \hat{x}^k, \quad (5.44)$$

where the derivatives of U should be understood as c -numbers (evaluated at $x = 0$), so that we may write

$$[\hat{p}_x, U(\hat{x})] = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k U}{\partial \hat{x}^k} [\hat{p}_x, \hat{x}^k] = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k U}{\partial \hat{x}^k} \left(\underbrace{\hat{p}_x \hat{x} \dots \hat{x}}_{k \text{ times}} - \underbrace{\hat{x} \hat{x} \dots \hat{x}}_{k \text{ times}} \hat{p}_x \right). \quad (5.45)$$

Applying Eq. (38) k times to the last term in the parentheses, exactly as we did it in Eq. (39), we get

$$[\hat{p}_x, U(\hat{x})] = -\sum_{k=1}^{\infty} \frac{1}{k!} \frac{\partial^k U}{\partial \hat{x}^k} i\hbar k \hat{x}^{k-1} = -i\hbar \sum_{k=1}^{\infty} \frac{1}{(k-1)!} \frac{\partial^k U}{\partial \hat{x}^k} \hat{x}^{k-1}. \quad (5.46)$$

But the last sum is just the Taylor expansion of the derivative $\partial U / \partial x$. Indeed,

$$\frac{\partial U}{\partial \hat{x}} = \sum_{k'=0}^{\infty} \frac{1}{k'!} \frac{\partial^{k'}}{\partial \hat{x}^{k'}} \left(\frac{\partial U}{\partial \hat{x}} \right) \hat{x}^{k'} = \sum_{k'=0}^{\infty} \frac{1}{k'!} \frac{\partial^{k'+1} U}{\partial \hat{x}^{k'+1}} \hat{x}^{k'} = \sum_{k=1}^{\infty} \frac{1}{(k-1)!} \frac{\partial^k U}{\partial \hat{x}^k} \hat{x}^{k-1}, \quad (5.47)$$

¹⁴ Since this Hamiltonian is time-independent, we may replace the partial derivative over time t with the full one.

where at the last step I have replaced the notation of the summation index from k' to $k - 1$. As a result, Eq. (43) yields:

$$\frac{d\hat{p}_x}{dt} = -\frac{\partial}{\partial \hat{x}} U(\hat{x}).$$

(5.48)

Heisenberg
equation
for
momentum

This equation again coincides with the classical equation of motion! Discussing spin dynamics in Sec. 4.6 and 5.1, we have already seen that this is very typical of the Heisenberg picture. Moreover, averaging Eqs. (42) and (48) over the initial state (as Eq. (4.191) prescribes¹⁵), we get similar results for the expectation values:¹⁶

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}, \quad \frac{d\langle p_x \rangle}{dt} = -\left\langle \frac{\partial U}{\partial x} \right\rangle.$$

(5.49)

Ehrenfest
theorem

However, it is important to remember that the equivalence between these quantum-mechanical equations and similar equations of classical mechanics is superficial, and the degree of the similarity between the two mechanics very much depends on the problem. As one extreme, let us consider the case when a particle's state, at any moment between t_0 and t , may be accurately represented by one, relatively narrow wave packet. Then we may interpret Eqs. (49) as equations of essentially classical motion for the wave packet's center, in accordance with the correspondence principle. However, even in this case it is important to remember about the purely quantum mechanical effects of nonvanishing wave packet width and its spreading in time, which were discussed in Sec. 2.2.

In the opposite extreme, Eqs. (49), though valid, may tell almost nothing about system's dynamics. Maybe the most apparent example is the “leaky” quantum well that was discussed in Sec. 2.5 - see Fig. 2.18 and its discussion. Since both the potential $U(x)$ and the initial state are symmetric relative to point $x = 0$, the right-hand parts of both Eqs. (49) identically equal zero. Of course, the result (that average values of both momentum and coordinate stay equal zero at all times) is correct, but it does not tell us too much about the rich dynamics of the system (the finite lifetime of the metastable state, the formation of two wave packets, their waveform and propagation speed), and about the important insight the solution gives for the quantum measurement theory. Another similar example is the band theory (Sec. 2.7), with its purely quantum effect of the allowed energy bands and forbidden gaps, of which Eq. (49) gives no clue.

To summarize, the Ehrenfest theorem is important as an illustration of the correspondence principle, but its predictive power should not be exaggerated.

Now we are ready to patch some holes left during our studies of wave mechanics in Chapters 1-3. First of all, I have promised you to develop a more balanced view at the monochromatic de Broglie waves (4.1), which would be more respectful to the evident $\mathbf{r} \leftrightarrow \mathbf{p}$ symmetry of the coordinate and momentum. Let us do this for the 1D case when the wave may be presented as¹⁷

¹⁵ Indeed, acting exactly as at derivation of Eq. (36), for a space-local Heisenberg operator we get

$$\langle A \rangle(t) = \int \Psi^*(x, t_0) \hat{A}_H(t, t_0) \Psi(x, t_0) dx.$$

¹⁶ The set of equations (49) constitute the Ehrenfest theorem.

¹⁷ From this point on, for the sake of brevity I will drop index x in the notation of the momentum – just as it was done in Chapter 2.

$$\psi_p(x) = a_p \exp\left\{i \frac{px}{\hbar}\right\}, \quad \text{for all } -\infty < x < +\infty. \quad (5.50)$$

Let us have a good look at this function. Since it satisfies equation (34) for the 1D momentum operator $\hat{p} = -i\hbar \partial / \partial x$,

$$\hat{p} \psi_p = p \psi_p, \quad (5.51)$$

ψ_p is an eigenfunction of the momentum operator. But this means that we can also write Eq. (6) for the corresponding ket-vector:

$$\hat{p}|p\rangle = p|p\rangle, \quad (5.52)$$

and according to Eq. (19) the wavefunction may be presented as

$$\psi_p(x) = \langle x|p\rangle. \quad (5.53)$$

Expression (53) is quite remarkable in its $x \leftrightarrow p$ symmetry - which may be pursued further on. Before doing that, however, we have to discuss normalization of such functions. Indeed, in this case, the probability density $w(x)$ (18) is constant, so that its integral

$$\int_{-\infty}^{+\infty} w(x) dx = \int_{-\infty}^{+\infty} \psi_p(x) \psi_p^*(x) dx \quad (5.54)$$

diverges if $a_p \neq 0$. Earlier in the course, we discussed two ways to avoid this divergence. One is to use a very large but finite integration volume – see Eq. (1.31). Another way to avoid the divergence is to form a wave packet of the type (2.20), possibly of a very large length and very narrow spread of momenta p . Then integral (54) may be required to equal 1 without any conceptual problem.

However, both these methods violate the $x \leftrightarrow p$ symmetry, and hence are inconvenient for our current purposes. Instead, let us continue to identify the bra- and ket-vectors $\langle a_A|$ and $|a_A\rangle$ of the general theory, developed in the beginning of this section, with eigenvectors $\langle p|$ and $|p\rangle$ of momentum – just as we have already done in Eq. (52). Then the normalization condition (9) becomes

$$\langle p|p'\rangle = \delta(p - p'). \quad (5.55)$$

Inserting the identity operator in the form (21) (with the integration variable x' replaced by x) into the left-hand side of this equation, we can translate this normalization rule to the wavefunction language:

$$\int dx \langle p|x\rangle \langle x|p'\rangle \equiv \int dx \psi_p^*(x) \psi_{p'}(x) = \delta(p - p'). \quad (5.56)$$

Now using Eq. (50), this requirement turns into the following condition:

$$a_p^* a_{p'} \int_{-\infty}^{+\infty} \exp\left\{i \frac{(p - p')x}{\hbar}\right\} dx \equiv |a_p|^2 2\pi\hbar \delta(p - p') = \delta(p - p'), \quad (5.57)$$

so that, finally, $a_p = \exp\{i\phi\}/(2\pi\hbar)^{1/2}$, where ϕ is an arbitrary (real) phase, and Eq. (50) becomes¹⁸

¹⁸ Repeating the calculation for each Cartesian component of a plane monochromatic wave of arbitrary dimensionality d , we get $\psi_{\mathbf{p}} = (2\pi\hbar)^{-d/2} \exp\{i(\mathbf{p}\cdot\mathbf{r}/\hbar + \phi)\}$.

$$\psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}} \exp\left\{i\left(\frac{px}{\hbar} + \phi\right)\right\}, \quad (5.58)$$

As was mentioned above, for finite-length wave packets such normalization is not really necessary. However, frequently it makes sense to keep the pre-exponential coefficient in Eq. (58) even for wave packets, because of the following reason. Let us form a wave packet of the type (2.20), based on wavefunctions (58) - taking $\phi = 0$ for the notation brevity, because it may be incorporated into function $\varphi(p)$:

$$\psi(x) = \frac{1}{(2\pi\hbar)^{1/2}} \int \varphi(p) \exp\left\{i\frac{px}{\hbar}\right\} dp. \quad (5.59)$$

From the mathematical point of view, this is just the equation of a 1D Fourier spatial transform, and its reciprocal is

$$\varphi(p) \equiv \frac{1}{(2\pi\hbar)^{1/2}} \int \psi(x) \exp\left\{-i\frac{px}{\hbar}\right\} dx. \quad (5.60)$$

Wave
packet
in reciprocal
representations

These expressions are completely symmetrical, and present the same wave packet; this is why functions $\psi(x)$ and $\varphi(p)$ are frequently called, respectively, the *coordinate* (x -) and *momentum* (p -) *representations* of the (same) state of the particle. Using Eqs. (53) and (58), they may be presented in an even more manifestly symmetric form,

$$\psi(x) = \int \varphi(p) \langle x|p \rangle dp, \quad \varphi(p) = \int \psi(x) \langle p|x \rangle dx, \quad (5.61)$$

in which the scalar products satisfy the basic postulate (4.14) of the bra-ket formalism:

$$\langle p|x \rangle = \frac{1}{(2\pi\hbar)^{1/2}} \exp\left\{-i\frac{px}{\hbar}\right\} = \langle x|p \rangle^*. \quad (5.62)$$

We already know that in the x -representation, i.e. in the usual wave mechanics, the coordinate operator $\hat{x}$ is reduced to the multiplication by x , and the momentum operator is proportional to a derivative over x :

$$\hat{x}|_{\text{in } x} = x, \quad \hat{p}|_{\text{in } x} = -i\hbar \frac{\partial}{\partial x}. \quad (5.63)$$

It is natural to guess that in the p -representation, the expressions for operators would be reciprocal:

$$\hat{x}|_{\text{in } p} = i\hbar \frac{\partial}{\partial p}, \quad \hat{p}|_{\text{in } p} = p, \quad (5.64)$$

Momentum
and coordinate
operators
in reciprocal
representations

with the difference in one sign only, due to the opposite signs of the Fourier exponents in Eqs. (59) and (60). The proof of Eqs. (64) is straightforward; for example, acting by the momentum operator to wavefunction (59), we get

$$\begin{aligned} \hat{p}\psi(x) &= -i\hbar \frac{\partial}{\partial x} \psi(x) = \frac{1}{(2\pi\hbar)^{1/2}} \int \varphi(p) \left(-i\hbar \frac{\partial}{\partial x} \exp\left\{i\frac{px}{\hbar}\right\} \right) dp \\ &= \frac{1}{(2\pi\hbar)^{1/2}} \int p \varphi(p) \exp\left\{i\frac{px}{\hbar}\right\} dp, \end{aligned} \quad (5.65)$$

and similarly for operator $\hat{x}$ acting on function $\varphi(p)$. Hence, the action of the operators (63) on wavefunction ψ (i.e. state's x -representation) gives the same results as the action of operators (64) on function φ (i.e. its p -representation).

It is interesting to have one more, different look at this coordinate-to-momentum duality. For that, notice that according to Eqs. (4.82)-(4.84), we may consider the bra-ket $\langle x|p\rangle$ as an element of the (infinite-size) matrix U_{xp} of the unitary transform from the x -basis to p -basis. Now let us derive the operator transform rule that would be a continuous version of Eq. (4.92). Say, we want to calculate a matrix element of some operator in the p -representation:

$$\langle p|\hat{A}|p'\rangle. \quad (5.66)$$

Inserting two identity operators (21) into this bra-ket, and then using Eq. (53) and its complex conjugate, and also Eq. (23) (again, valid only for space-local operators!), we get

$$\begin{aligned} \langle p|\hat{A}|p'\rangle &= \int dx \int dx' \langle p|x\rangle \langle x|\hat{A}|x'\rangle \langle x'|p'\rangle = \int dx \int dx' \psi_p^*(x) \langle x|\hat{A}|x'\rangle \psi_{p'}(x') \\ &= \frac{1}{2\pi\hbar} \int dx \int dx' \exp\left\{-i\frac{px}{\hbar}\right\} \delta(x-x') \hat{A} \exp\left\{i\frac{p'x'}{\hbar}\right\} = \frac{1}{2\pi\hbar} \int dx \exp\left\{-i\frac{px}{\hbar}\right\} \hat{A} \exp\left\{i\frac{p'x}{\hbar}\right\}. \end{aligned} \quad (5.67)$$

For example, for the momentum operator itself, this relation yields:

$$\langle p|\hat{p}|p'\rangle = \frac{1}{2\pi\hbar} \int dx \exp\left\{-i\frac{px}{\hbar}\right\} \left(-i\hbar \frac{\partial}{\partial x}\right) \exp\left\{i\frac{p'x}{\hbar}\right\} = \frac{p'}{2\pi\hbar} \int_{-\infty}^{+\infty} \exp\left\{i\frac{(p'-p)x}{\hbar}\right\} dx = p'\delta(p'-p). \quad (5.68)$$

Due to Eq. (52), this result is equivalent to the second of Eqs. (64).

A natural question arises: why is the momentum representation used much less frequently than the coordinate representation - i.e., the wave mechanics? The answer is purely practical: besides the special case of the harmonic oscillator (to be revisited in Sec. 4 below), the orbital motion Hamiltonian (31) is not $x \leftrightarrow p$ symmetric, with the potential energy $U(x)$ being typically a more complex function than the kinetic energy, which is quadratic in momentum. Because of that, it is easier for problem solution to keep the potential energy operator just a wavefunction multiplier, as it is in the coordinate representation.

The most significant exception of this rule is the motion in a periodic potential, especially in the presence of additional external force $F(t)$, which may result in the effects discussed in Secs. 2.8 and 2.9 (the Bloch oscillations, Landau-Zener tunneling etc.). Indeed, in this case the dispersion relation $E_n(q)$, typically rather involved, plays the role of the effective kinetic energy, while the effective potential energy $U_{\text{ef}} = -F(t)x$ in the field of the additional force is a simple function of x . This is why discussions of the listed and more complex issues of the band theory (such as quasiparticle scattering, mobility, diffusion, etc.) in solid state physics theory are most typically based on the momentum representation.

5.3. Feynman's path integrals

As has been already mentioned, even within the realm of wave mechanics, the bra-ket language allows to streamline some calculations that would be very bulky using the notation used in Chapters 1-3. Probably the best example in the famous alternative, *path integral* formulation of quantum mechanics,

developed in 1948 by R. Feynman.¹⁹ I will review this important concept - admittedly cutting one math corner for brevity.²⁰ (This shortcut will be clearly marked.)

Let us inner-multiply both parts of Eq. (4.157), which is essentially the definition of the time-evolution operator, by the bra-vector of state x ,

$$\langle x | \alpha(t) \rangle = \langle x | \hat{u}(t, t_0) | \alpha(t_0) \rangle, \quad (5.69)$$

insert the identity operator before the ket-vector in the right-hand part, and then use the closure condition in the form of Eq. (21), with x' replaced with x_0 :

$$\langle x | \alpha(t) \rangle = \int dx_0 \langle x | \hat{u}(t, t_0) | x_0 \rangle \langle x_0 | \alpha(t_0) \rangle. \quad (5.70)$$

According to Eq. (19), this equality may be presented as

$$\Psi_\alpha(x, t) = \int dx_0 \langle x | \hat{u}(t, t_0) | x_0 \rangle \Psi_\alpha(x_0, t_0). \quad (5.71)$$

Comparing this expression with Eq. (2.44), we see that the bra-ket in this relation is nothing else than the 1D propagator, which was discussed in Sec. 2.2:

$$\langle x | \hat{u}(t, t_0) | x_0 \rangle = G(x, t; x_0, t_0). \quad (5.72)$$

As a reminder, we have already calculated the propagator for a free particle – see Eq. (2.49).

Now let us break the time segment $[t_0, t]$ into N (for the time being, not necessarily equal) parts by inserting $(N-1)$ intermediate points (Fig. 2)

$$t_0 < t_1 < \dots < t_k < \dots < t_{N-1} < t, \quad (5.73)$$

and rewrite the time evolution operator in the form

$$\hat{u}(t, t_0) = \hat{u}(t, t_{N-1}) \hat{u}(t_{N-1}, t_{N-2}) \dots \hat{u}(t_2, t_1) \hat{u}(t_1, t_0), \quad (5.74)$$

whose correctness is evident from the very definition (4.157) of the operator. Plugging Eq. (74) into Eq. (72), let us insert the identity operator, again in the form (21) but written for x_k rather than x' , between each two partial evolution operators including time argument t_k . The result is

$$G(x, t; x_0, t_0) = \int dx_{N-1} \int dx_{N-2} \dots \int dx_1 \langle x | \hat{u}(t, t_{N-1}) | x_{N-1} \rangle \langle x_{N-1} | \hat{u}(t_{N-1}, t_{N-2}) | x_{N-2} \rangle \dots \langle x_1 | \hat{u}(t_1, t_0) | x_0 \rangle. \quad (5.75)$$

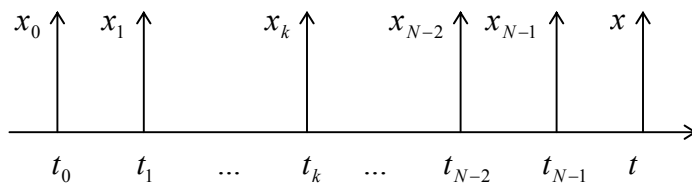


Fig. 5.2. Time partition and coordinate notation at the initial stage of the Feynman's path integral derivation.

¹⁹ According to Feynman's memories, his work was motivated by a "mysterious" remark by P. A. M. Dirac in his pioneering 1930 textbook on quantum mechanics.

²⁰ For a more thorough discussion of the path-integral approach, see the famous text R. Feynman and A. Hibbs, *Quantum Mechanics and Path Integrals* first published in 1965. (For its latest edition by Dover in 2010, the book was emended by D. Styler.) For a more recent monograph that reviews more applications, see L. Schulman, *Techniques and Applications of Path Integration*, Wiley, 1981.

The physical sense of each integration variable x_k is the wavefunction's argument at time t_k - see Fig. 2. The key Feynman's breakthrough was the realization that if all intervals are similar and sufficiently small, $t_k - t_{k-1} = d\tau \rightarrow 0$, all the partial bra-kets participating in Eq. (75) may be readily expressed via Eq. (2.49), even if the particle is not free, but moves in a stationary potential profile $U(x)$. To show that, let us use either Eq. (4.175) or Eq. (4.181), which, for a small time interval $d\tau$, give the same result:

$$\hat{u}(\tau + d\tau, \tau) = \exp\left\{-\frac{i}{\hbar} \hat{H} d\tau\right\} = \exp\left\{-\frac{i}{\hbar} \left(\frac{\hat{p}^2}{2m} d\tau + U(\hat{x}) d\tau\right)\right\}. \quad (5.76)$$

Generally, an exponent of a sum of two operators may be treated as that of c -number arguments, and in particular factored into a product of two exponents, only if the operators commute. (Indeed, in this case we can use all the standard algebra for exponents of c -number arguments.) In our case, this is not so, because operator $\hat{p}$ does not commute with $\hat{x}$, and hence with $U(\hat{x})$. However, it may be shown²¹ that for an infinitesimal time interval $d\tau$, the nonvanishing commutator

$$\left[\frac{\hat{p}^2}{2m} d\tau, U(\hat{x}) d\tau\right] \neq 0, \quad (5.77)$$

proportional to $(d\tau)^2$, is so small that in the first approximation in $d\tau$ its effects may be ignored. As a result, we may factor the right-hand part in Eq. (76) by writing

$$\hat{u}(\tau + d\tau, \tau)_{d\tau \rightarrow 0} \rightarrow \exp\left\{-\frac{i}{\hbar} \frac{\hat{p}^2}{2m} d\tau\right\} \exp\left\{-\frac{i}{\hbar} U(\hat{x}) d\tau\right\}. \quad (5.78)$$

(This approximation is very much similar in spirit to the rectangle-formula approximation for a usual 1D integral, which is also asymptotically impeachable.)

Since the second exponential function in the right-hand part of Eq. (78) commutes with the coordinate operator, we can move it out of each partial bra-ket participating in Eq. (75), with $U(x)$ turning into a c -number function:

$$\langle x_{\tau+d\tau} | \hat{u}(\tau + d\tau, \tau) | x_\tau \rangle = \langle x_{\tau+d\tau} | \exp\left\{-\frac{i}{\hbar} \frac{\hat{p}^2}{2m} d\tau\right\} | x_\tau \rangle \exp\left\{-\frac{i}{\hbar} U(x) d\tau\right\}. \quad (5.79)$$

But the remaining bra-ket is just the propagator of a free particle, and we can use Eq. (2.49) for it:

$$\langle x_{\tau+d\tau} | \exp\left\{-\frac{i}{\hbar} \frac{\hat{p}^2}{2m} d\tau\right\} | x_\tau \rangle = \left(\frac{m}{2\pi i \hbar d\tau}\right)^{1/2} \exp\left\{i \frac{m(dx)^2}{2\hbar d\tau}\right\}. \quad (5.80)$$

As the result, the full propagator (75) takes the form

$$G(x, t; x_0, t_0) = \lim_{\substack{d\tau \rightarrow 0 \\ N \rightarrow \infty}} \int dx_{N-1} \int dx_{N-2} \dots \int dx_1 \left(\frac{m}{2\pi i \hbar d\tau}\right)^{N/2} \exp\left\{\sum_{k=1}^N \left[i \frac{m(dx)^2}{2\hbar d\tau} - i \frac{U(x)}{\hbar} d\tau\right]\right\}. \quad (5.81)$$

²¹ A strict proof of this intuitively evident statement would take more space and time than I can afford.

At $N \rightarrow \infty$ and hence $d\tau \equiv (t - t_0)/N \rightarrow 0$, the sum under the exponent in this expression tends to an integral:

$$\sum_{k=1}^N \frac{i}{\hbar} \left[\frac{m}{2} \left(\frac{dx}{d\tau} \right)^2 - U(x) \right]_{\tau=t_k} d\tau \rightarrow \frac{i}{\hbar} \int_{t_0}^t \left[\frac{m}{2} \left(\frac{dx}{d\tau} \right)^2 - U(x) \right] d\tau, \quad (5.82)$$

and the expression in square brackets is just the particle's Lagrangian function L .²² The integral of the function over time is the classical action $\mathcal{S}$ calculated along a particular “path” $x(\tau)$.²³ As a result, defining the (1D) *path integral* as

$$\int (...) D[x(\tau)] \equiv \lim_{\substack{d\tau \rightarrow 0 \\ N \rightarrow \infty}} \left(\frac{m}{2\pi i \hbar d\tau} \right)^{N/2} \int dx_{N-1} \int dx_{N-2} \dots \int dx_1 (...), \quad (5.83a)$$

1D path
integral:
definition

we can bring our result to a superficially simple form

$$G(x, t; x_0, t_0) = \int \exp \left\{ \frac{i}{\hbar} \mathcal{S}[x(\tau)] \right\} D[x(\tau)]. \quad (5.83b)$$

1D
propagator
via path
integral

The name “path integral” for the mathematical construct (83a) may be readily explained if we keep the number N of time intervals large but finite, and also approximate each of the enclosed integrals by a sum over $M \gg 1$ discrete points along the coordinate axis (Fig. 3a).

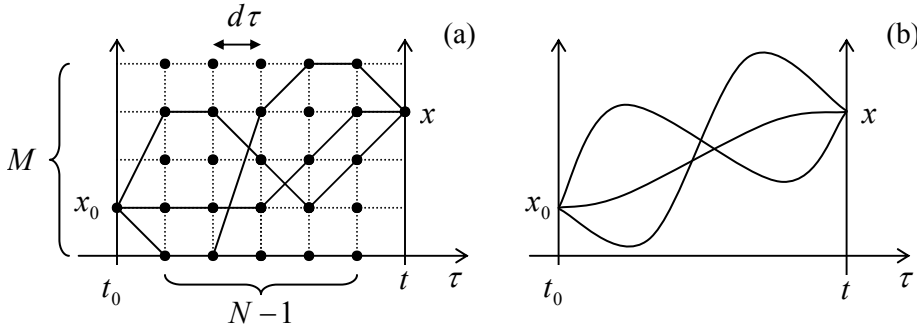


Fig. 5.3. Several 1D classical paths in (a) the discrete approximation and (b) the continuous limit.

Then the path integral is a product of $(N - 1)$ sums corresponding to different values of time τ , each of them with M terms, each of the terms representing the function under the integral at a particular spatial point. Multiplying those $(N - 1)$ sums, we get a sum of $(N - 1)M$ terms, each evaluating the function at a specific spatial-temporal point $[x, \tau]$. These terms may be now grouped to represent all possible different continuous classical paths $x[\tau]$ from the initial point $[x_0, t_0]$ to the finite point $[x, t]$. It is evident that the last interpretation remains true even in the continuous limit $N, M \rightarrow \infty$ – see Fig. 3b.

Why does such representation of the sum has sense? This is because in the classical limit the particle follows just a certain path, corresponding to the minimum of action $\mathcal{S}$.²² Hence, for all close trajectories, the difference $(\mathcal{S} - \mathcal{S}_{cl})$ is proportional to the square of the deviation from the classical trajectory. Hence, for a quasiclassical motion, with $\mathcal{S}_{cl} \gg \hbar$, there is a substantial bunch of close trajectories, with $(\mathcal{S} - \mathcal{S}_{cl}) \ll \hbar$, that give similar contributions to the path integral. On the other hand,

²² See, e.g., CM Sec. 2.1.

²³ See, e.g., CM Sec. 9.2.

strongly non-classical trajectories, with $(\mathcal{S} - \mathcal{S}_{cl}) \gg \hbar$, give phases $\mathcal{S}/\hbar$ rapidly oscillating from one trajectory to the next one, and their contributions to the path integral are averaged out.²⁴ As a result, for the quasiclassical motion, the propagator's exponent may be evaluated on the classical path:

$$G_{cl} \propto \exp\left\{\frac{i}{\hbar} \mathcal{S}_{cl}\right\} = \exp\left\{\frac{i}{\hbar} \int_{t_0}^t \left[\frac{m}{2} \left(\frac{dx}{d\tau} \right)^2 - U(x) \right] d\tau\right\}. \quad (5.84)$$

The sum of the kinetic and potential energies is the full energy E of the particle, that remains constant for motion in a stationary potential $U(x)$, so that we may rewrite the expression under the integral as²⁵

$$\left[\frac{m}{2} \left(\frac{dx}{d\tau} \right)^2 - U(x) \right] d\tau = \left[m \left(\frac{dx}{d\tau} \right)^2 - E \right] d\tau = m \frac{dx}{d\tau} dx - E d\tau. \quad (5.85)$$

With that replacement, Eq. (83b) yields

$$G_{cl} \propto \exp\left\{\frac{i}{\hbar} \int_{x_0}^x m \frac{dx}{d\tau} dx\right\} \exp\left\{-\frac{i}{\hbar} E(t - t_0)\right\} = \exp\left\{\frac{i}{\hbar} \int_{x_0}^x p(x) dx\right\} \exp\left\{-\frac{i}{\hbar} E(t - t_0)\right\}, \quad (5.86)$$

where p is the classical momentum of the particle. But (at least, leaving the pre-exponential factor alone) this is exactly the WKB approximation result that was derived and studied in detail in Chapter 2!

One may question the value of a calculation that yields the results that could be readily obtained from Schrödinger's wave mechanics. The Feynman's approach, is indeed not used too often, but it has its merits. First, it has an important philosophical (and hence heuristic) value. Indeed, Eq. (83) may be interpreted by saying that the essence of quantum mechanics is the exploration, by the system, of all possible paths $x(\tau)$, each of them classical-like in the sense that the particle's coordinate x and velocity $dx/d\tau$ (and hence its momentum) are exactly defined simultaneously at each point. The resulting contributions to the path integral are added up coherently to form the final propagator G , and via it, the final probability $W \propto |G|^2$ of the particle propagation from $[x_0, t_0]$ to $[x, t]$. Of course, as the scale of action (i.e. of the energy-by-time product) of the motion decreases and becomes comparable to $\hbar$, more and more paths produce substantial contribution to this sum, and hence to W , ensuring a larger and larger difference between the quantum and classical properties of the system.

Second, the path integral provides a justification for some simple explanations of quantum phenomena. A typical example is the quantum interference effects discussed in Sec. 3.1 – see, e.g., Fig. 3.1 and the corresponding text. At that discussion, we used the Huygens principle to argue that at the two-slit interference, the WKB approximation might be restricted of effects by two paths that pass through different slits, but otherwise consisting of straight-line segments. To have another look at that assumption, let us generalize the path integral to multi-dimensional geometries. Fortunately, the simple structure of Eq. (83b) makes such generalization virtually evident:

²⁴ This fact may be proved by expanding the difference $(\mathcal{S} - \mathcal{S}_{cl})$ in the Taylor series in path variations (leaving only the leading quadratic terms) and working out the resulting Gaussian integrals. It is interesting that the integration, together with the pre-exponential coefficient in Eq. (83a), gives exactly the pre-exponential factor that we have already found in Sec. 2.4 when refining the WKB approximation.

²⁵ The same trick is often used in analytical classical mechanics – say, for proving the Hamilton principle, and for the derivation of the Hamilton – Jacobi equations (see, e.g. CM Secs. 10.3-4).

$$G(\mathbf{r}, t; \mathbf{r}_0, t_0) = \int \exp\left\{\frac{i}{\hbar} \mathcal{S}[\mathbf{r}(\tau)]\right\} D[\mathbf{r}(\tau)],$$

$$\mathcal{S} \equiv \int_{t_0}^t L\left(\mathbf{r}, \frac{d\mathbf{r}}{d\tau}\right) d\tau = \int_{t_0}^t \left[\frac{m}{2} \left(\frac{d\mathbf{r}}{d\tau} \right)^2 - U(\mathbf{r}) \right] d\tau. \quad (5.87)$$

3D
propagator
via the path
integral

where definition (83a) of the path integral should be also modified correspondingly. (I will not go into these technical details.) For the Young-type experiment (Fig. 3.1), where a classical particle could reach the detector only after passing through one of the slits, the classical paths are the straight-line segments shown in Fig. 3.1, and if they are much longer than the de Broglie wavelength, the propagator may be well approximated by the sum of two integrals of $L d\tau = i\mathbf{p}(\mathbf{r}) \cdot d\mathbf{r} / \hbar$ - as it was done in Sec. 3.1.

Last but not least, the path integral allows simple solutions of some problems that would be hard to get by other methods. As the simplest example, let us consider the problem of tunneling in multi-dimensional space, sketched in Fig. 4 for the 2D case - just for graphics' simplicity. Here, potential $U(x, y)$ has the “saddle” shape. (Another helpful image is a mountain path between two summits, in Fig. 4 located on the top and at the bottom of the drawing.) A particle of energy E may move classically in the left and right regions with $U(x, y) < E$, but can pass from one of these regions to another one only via the quantum-mechanical tunneling under the pass. Let us calculate the transparency of this tunnel barrier in the WKB approximation, ignoring the possible pre-exponential factor.

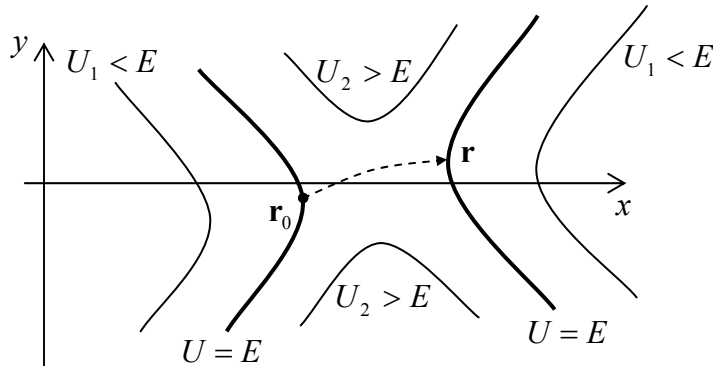


Fig. 5.4. Saddle-type 2D potential profile and the instanton trajectory of a particle of energy E (dashed line, schematically).

According to the evident multi-dimensional generalization Eq. (86), for the classically forbidden region, where $E < U(x, y)$, the contributions to propagator (87) are proportional to

$$\exp\left\{-\int_{\mathbf{r}_0}^{\mathbf{r}} \boldsymbol{\kappa}(\mathbf{r}) \cdot d\mathbf{r}\right\} \exp\left\{-\frac{i}{\hbar} E(t - t_0)\right\}, \quad (5.88)$$

where the magnitude of vector $\boldsymbol{\kappa}$ at each point may be calculated just in the 1D case - see, e.g., Eq. (2.97),

$$\frac{\hbar^2 \kappa^2(\mathbf{r})}{2m} = U(\mathbf{r}) - E, \quad (5.89)$$

while its direction should be tangential to the path trajectory in space. Now the path integral is actually much simpler than in the classically-allowed region, because the spatial exponents are purely real and there is no complex interference between them. Because of the minus sign in the exponent, the *largest*

contribution to G evidently comes from the trajectory (or rather a narrow bundle of trajectories) for which the functional

$$\int_{\mathbf{r}_0}^{\mathbf{r}} \boldsymbol{\kappa}(\mathbf{r}') \cdot d\mathbf{r}' \quad (5.90)$$

has the *smallest* value, and the barrier transmission coefficient may be calculated as

3D
tunneling
in WKB
limit

$$T \approx |G|^2 \approx \exp \left\{ -2 \int_{\mathbf{r}_0}^{\mathbf{r}} \boldsymbol{\kappa}(\mathbf{r}') \cdot d\mathbf{r}' \right\}, \quad (5.91)$$

where $\mathbf{r}$ and $\mathbf{r}_0$ are certain points on the opposite classical turning-point surfaces: $U(\mathbf{r}) = U(\mathbf{r}_0) = E$.²⁶

Thus the tunneling problem is reduced to finding the trajectory (including points $\mathbf{r}$ and $\mathbf{r}_0$) that connects the two surfaces and minimizes functional (90). This is of course a well-known problem of the calculus of variations,²⁷ but it is interesting that the path integral provides a simple alternative way of solving it. Let us consider an auxiliary problem of particle's motion in a potential profile $U_{\text{inv}}(\mathbf{r})$ that is inverted relative to particle's energy E , i.e. is defined by the following equality:

$$U_{\text{inv}}(\mathbf{r}) - E \equiv E - U(\mathbf{r}). \quad (5.92)$$

As was discussed above, at fixed energy E , the path integral for the WKB motion in the classically allowed region of potential $U_{\text{inv}}(x, y)$ (that coincides with the classically forbidden region of the original problem) is dominated by the classical trajectory corresponding to the minimum of

$$\mathcal{S}_{\text{inv}} = \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{p}_{\text{inv}}(\mathbf{r}') \cdot d\mathbf{r}' = \hbar \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{k}_{\text{inv}}(\mathbf{r}') \cdot d\mathbf{r}', \quad (5.93)$$

where $\mathbf{k}_{\text{inv}}$ should be determined from the relation

$$\frac{\hbar^2 k_{\text{inv}}^2(\mathbf{r})}{2m} \equiv E - U_{\text{inv}}(\mathbf{r}). \quad (5.94)$$

But comparing Eqs. (89), (92), and (94), we see that $\mathbf{k}_{\text{inv}} = \boldsymbol{\kappa}$ at each point of space! This means that the tunneling path (in the WKB limit) corresponds to the classical (so-called *instanton*)²⁸ trajectory of the same particle in the inverted potential $U_{\text{inv}}(\mathbf{r})$. If the initial point $\mathbf{r}_0$ is fixed, this trajectory may be readily found by the means of classical mechanics. (Note that the initial velocity of the instanton launched from point $\mathbf{r}_0$ should be zero, because by the classical turning point definition: $U_{\text{inv}}(\mathbf{r}_0) = U(\mathbf{r}_0) = E$.) Thus the problem is reduced to a simpler task of maximizing the transparency (91) over the position of $\mathbf{r}_0$ on the equipotential surface $U(\mathbf{r}_0) = E$. Moreover, for many symmetric potentials, the position of this point may be readily guessed without calculations.

²⁶ One can argue that the pre-exponential coefficient in Eq. (91) should be close to 1, just like in Eq. (2.117), especially if the potential is smooth in the sense of Eq. (2.107), where x is the coordinate along the trajectory.

²⁷ For a concise introduction to the field see, e.g., I. Gelfand and S. Fomin, *Calculus of Variations*, Dover, 2000, or L. Elsgolc, *Calculus of Variations*, Dover, 2007.

²⁸ In quantum field theory, the instanton concept may be formulated somewhat differently, and has more complex applications - see, e.g. R. Rajaraman, *Solitons and Instantons*, North Holland, 1987.

Note that besides the calculation of barrier transparency, the instanton trajectory has one more important implication: the so-called *traversal time* τ_t of the classical motion along it, in the inverted potential, defined by Eq. (94), plays the role of the most important (though not the only one) time scale of particle's tunneling under the potential barrier.²⁹

5.4. Revisiting harmonic oscillator

Let us return to the 1D harmonic oscillator, i.e. any system described by Hamiltonian (2.50) with potential energy (2.111):

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega_0^2 \hat{x}^2}{2}. \quad (5.95)$$

Harmonic
oscillator:
Hamiltonian

In Sec. 2.10 we have used the “brute-force” (wave-mechanics) approach to analyze the eigenfunctions $\psi_n(x)$ and eigenvalues E_n of this Hamiltonian, and found that, unfortunately, that approach required relatively complex math that obscures the physics of these stationary (“Fock”) states. Now let us use the bra-ket formalism to make the properties of these states much more transparent, using very simple calculations.

First, introducing normalized (dimensionless) operators of coordinates and momentum:³⁰

$$\hat{\xi} \equiv \frac{\hat{x}}{x_0}, \quad \hat{\zeta} \equiv \frac{\hat{p}}{m\omega_0 x_0}, \quad (5.96)$$

where $x_0 \equiv (\hbar/m\omega_0)^{1/2}$ is the natural coordinate scale ($\sqrt{2}$ the r.m.s. spread of ground-state wavefunction) which was discussed in detail in Sec. 2.10, we can present Hamiltonian (95) in a very simple and $x \leftrightarrow p$ symmetric form:

$$\hat{H} = \frac{\hbar\omega_0}{2} (\hat{\xi}^2 + \hat{\zeta}^2). \quad (5.97)$$

Now, let us introduce a new operator

$$\hat{a} \equiv \frac{1}{\sqrt{2}} (\hat{\xi} + i\hat{\zeta}) = \left(\frac{m\omega_0}{2\hbar} \right)^{1/2} \left(\hat{x} + i \frac{\hat{p}}{m\omega_0} \right). \quad (5.98a)$$

Since both operators $\hat{\xi}$ and $\hat{\zeta}$ correspond to real observables, i.e. have real eigenvalues and hence are Hermitian (self-adjoint), the Hermitian conjugate of operator $\hat{a}$ is simply its complex conjugate:

Creation-
annihilation
operators:
definition

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} (\hat{\xi} - i\hat{\zeta}) = \left(\frac{m\omega_0}{2\hbar} \right)^{1/2} \left(\hat{x} - i \frac{\hat{p}}{m\omega_0} \right), \quad (5.98b)$$

Solving the system of two equations (98) for $\hat{\xi}$ and $\hat{\zeta}$, we may readily get reciprocal relations

²⁹ See, e.g., M. Buttiker and R. Landauer, *Phys. Rev. Lett.* **49**, 1739 (1982), and references therein.

³⁰ This normalization is not really necessary, it just makes the following calculations less bulky - and thus more aesthetically appealing.

$$\hat{\xi} = \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger), \quad \hat{\zeta} = \frac{1}{\sqrt{2}i}(\hat{a} - \hat{a}^\dagger). \quad (5.99)$$

Our Hamiltonian (97) includes squares of these operators. Calculating them, we have to be careful to avoid swapping the new operators, because they do not commute. Indeed, for the normalized operators (96), Eq. (2.14) gives

$$[\hat{\xi}, \hat{\zeta}] = \frac{1}{x_0^2 m \omega_0} [\hat{x}, \hat{p}] = i\hat{I}, \quad (5.100)$$

so that Eqs. (98) yield

Creation-
annihilation
operators:
commutation
relation

$$[\hat{a}, \hat{a}^\dagger] = \frac{1}{2} [(\hat{\xi} + i\hat{\zeta})(\hat{\xi} - i\hat{\zeta})] = -\frac{i}{2} ([\hat{\xi}, \hat{\zeta}] - [\hat{\zeta}, \hat{\xi}]) = \hat{I}. \quad (5.101)$$

With such due caution, Eq. (99) gives

$$\hat{\xi}^2 = \frac{1}{2}(\hat{a}^2 + \hat{a}^{\dagger 2} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}), \quad \hat{\zeta}^2 = -\frac{1}{2}(\hat{a}^2 + \hat{a}^{\dagger 2} - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}). \quad (5.102)$$

Plugging these expressions back into Eq. (97), we get

$$\hat{H} = \frac{\hbar\omega_0}{2}(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}). \quad (5.103)$$

This expression is elegant enough, but may be recast into an even more convenient form. For that, let us rewrite the commutation relation (100) as

$$\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + \hat{I}, \quad (5.104)$$

and plug it into Eq. (103). The result is

$$\hat{H} = \frac{\hbar\omega_0}{2}(2\hat{a}^\dagger\hat{a} + \hat{I}) = \hbar\omega_0\left(\hat{N} + \frac{1}{2}\hat{I}\right), \quad (5.105)$$

Hamiltonian
and number
operators

where, in the last form, one more (evidently, Hermitian) operator,

$$\hat{N} \equiv \hat{a}^\dagger\hat{a}, \quad (5.106)$$

has been introduced. Since, according to Eq. (105), operators $\hat{H}$ and $\hat{N}$ differ only by the addition of an identity operator and the multiplication by a c -number, these operators commute. Hence, according to the general arguments of Sec. 4.5, they share the set of stationary (Fock) eigenstates n , and we can write the eigenproblem for the new operator as

$$\hat{N}|n\rangle = N_n|n\rangle, \quad (5.107)$$

where N_n are some eigenvalues that, according to Eq. (105), determine also the energy spectrum of the oscillator:

$$E_n = \hbar\omega_0\left(N_n + \frac{1}{2}\right). \quad (5.108)$$

So far, we know only that all eigenvalues N_n are real, but not much more. In order to calculate them, let us carry out the following calculation - splendid in its simplicity and efficiency. Consider the result of action of operator $\hat{N}$ on the ket-vector $\hat{a}^\dagger|n\rangle$. Using the definition (106) and the associative rule, we may write

$$\hat{N}(\hat{a}^\dagger|n\rangle) = (\hat{a}^\dagger\hat{a})(\hat{a}^\dagger|n\rangle) = \hat{a}^\dagger(\hat{a}\hat{a}^\dagger)|n\rangle. \quad (5.109)$$

Now using the commutation relation (104), and then Eq. (107), we may continue as

$$\hat{a}^\dagger(\hat{a}\hat{a}^\dagger)|n\rangle = \hat{a}^\dagger(\hat{a}^\dagger\hat{a} + \hat{I})|n\rangle = \hat{a}^\dagger(\hat{N} + \hat{I})|n\rangle = \hat{a}^\dagger(N_n + 1)|n\rangle = (N_n + 1)(\hat{a}^\dagger|n\rangle). \quad (5.110)$$

Let us summarize the result of this calculation:

$$\hat{N}(\hat{a}^\dagger|n\rangle) = (N_n + 1)(\hat{a}^\dagger|n\rangle). \quad (5.111)$$

Performing an absolutely similar calculation with operator $\hat{a}$, we can also get another formula:

$$\hat{N}(\hat{a}|n\rangle) = (N_n - 1)(\hat{a}|n\rangle). \quad (5.112)$$

It is time to stop calculations and translate these results into plain English: if $|n\rangle$ is an eigenket of operator $\hat{N}$ with eigenvalue N_n , then $\hat{a}^\dagger|n\rangle$ and $\hat{a}|n\rangle$ are also eigenkets of that operator, with eigenvalues $(N_n + 1)$, and $(N_n - 1)$, respectively. This statement may be presented with the *ladder diagram* shown in Fig. 5.

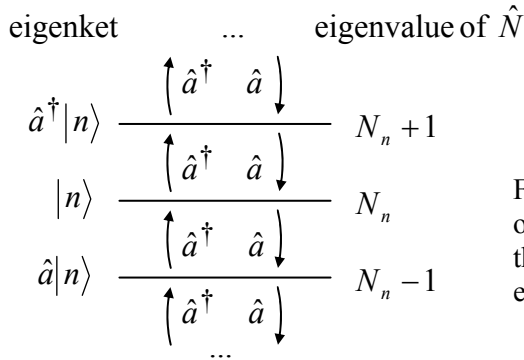


Fig. 5.5. Hierarchy (the “ladder diagram”) of eigenstates of a 1D harmonic oscillator. Arrows show the actions of the creation and annihilation operators on the eigenstates.

Operator $\hat{a}^\dagger$ moves the system a step up the ladder, while operator $\hat{a}$ brings it one step down. In other words, the former operator creates a new *excitation* of the system,³¹ while the latter operator kills (“annihilates”) such excitation. This is why $\hat{a}^\dagger$ is called the *creation operator*, and $\hat{a}$, the *annihilation operator*. In its turn, according to Eq. (107), operator $\hat{N}$ does not change the state of the system, but “counts” its position on the ladder:

$$\langle n|\hat{N}|n\rangle = \langle n|N_n|n\rangle = N_n. \quad (5.113)$$

³¹ For the electromagnetic field oscillators, such excitations are called *photons*; for the mechanical wave field oscillators, *phonons*, etc.

This is why $\hat{N}$ is called the *number operator*, in our current context meaning the number of the elementary excitations of the oscillator.

This calculation still needs a completion. Indeed, we still do not know whether the ladder shown in Fig. 5 shows *all* eigenstates of the oscillator, and what exactly the numbers N_n are. Fascinating enough, both questions may be answered by exploring a single paradox. Let us start with some state (step of the ladder), and keep going down it, applying operator $\hat{a}$ again and again. Each time, eigenvalue N_n is decreased by one, so that eventually it should become negative. However, this cannot happen, because any real eigenstate, including the states presented by kets $|d\rangle \equiv \hat{a}|n\rangle$ and $|n\rangle$, should have a positive norm – see Eq. (4.16). Comparing the norms,

$$\|n\|^2 = \langle n|n\rangle, \quad \|d\|^2 = \langle n|\hat{a}^\dagger \hat{a}|n\rangle = \langle n|\hat{N}|n\rangle = N_n \langle n|n\rangle, \quad (5.114)$$

we see that the both of them cannot be positive simultaneously if N_n is negative.

The way toward the resolution of this paradox is to notice that the action of the creation and annihilation operators on the stationary states may consist in not only their promotion to the next step of the ladder diagram, but also by their multiplication by some *c*-numbers:

$$\hat{a}|n\rangle = A_n|n-1\rangle, \quad \hat{a}^\dagger|n\rangle = A'_n|n+1\rangle. \quad (5.115)$$

(Linear relations (111) and (112) clearly allow that.) Let us calculate coefficients A_n assuming, for convenience, that all eigenstates, including states n and $(n-1)$, are normalized:

$$\langle n|n\rangle = 1, \quad \langle n-1|n-1\rangle = \langle n|\frac{\hat{a}^\dagger}{A_n^*}\frac{\hat{a}}{A_n}|n\rangle = \frac{1}{A_n^* A_n} \langle n|\hat{N}|n\rangle = \frac{N_n}{A_n^* A_n} \langle n|n\rangle = 1. \quad (5.116)$$

From here, we get $|A_n| = (N_n)^{1/2}$, i.e.

$$\hat{a}|n\rangle = N_n^{1/2} e^{i\varphi_n} |n-1\rangle, \quad (5.117)$$

where φ_n is an arbitrary real phase. Now let us consider what happens if all numbers N_n are integers. (Because of the definition of N_n , given by Eq. (107), it is convenient to call these integers n , i.e. by the same letter as the corresponding eigenstate.) Then when we have come down to state with $n = 0$, an attempt to make one more step down gives

$$\hat{a}|0\rangle = 0|-1\rangle. \quad (5.118)$$

But in accordance with Eq. (4.9), the state in the right-hand part of this equation is the “null-state”, i.e. does not exist.³² This gives the (only known :-) resolution of the state ladder paradox: the ladder has the lowest step with $N_n = n = 0$.

As a by-product of our discussion, we have obtained a very important relation $N_n = n$, which means, in particular, that the state ladder includes *all* eigenstates of the oscillator. Plugging this relation into Eq. (108), we see that the *full* spectrum of eigenenergies of the harmonic oscillator is described by the simple formula

³² Please note again the radical difference between the null-state in the right-hand part of Eq. (118) and the state described by ket-vector $|0\rangle$ in the left-hand side of that relation. The latter state *does* exist and, moreover, presents the most important, ground state of the system, with $n = 0$ - see Eq. (2.269).

$$E_n = \hbar\omega_0 \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots, \quad (5.119)$$

which was already discussed in Sec. 2.10. It is rather remarkable that the bra-ket formalism has allowed us to derive it without calculation of the corresponding (rather cumbersome) wavefunctions $\psi_n(x)$ – see Eqs. (2.279).

Moreover, the formalism may be also used to calculate virtually any bra-ket pertaining to the oscillator, without using $\psi_n(x)$. In order to illustrate that, let us first calculate A'_n participating in the latter of relations (115). This can be done absolutely similarly to the above calculation of A_n ; otherwise, since we already know that $|A_n| = (N_n)^{1/2} = n^{1/2}$, we may notice that according to Eqs. (106) and (115), the eigenproblem (107), that in our new notation for N_n becomes

$$\hat{N}|n\rangle = n|n\rangle, \quad (5.120)$$

may be rewritten as

$$n|n\rangle = \hat{a}^\dagger \hat{a}|n\rangle = \hat{a}^\dagger A_n|n-1\rangle = A_n A'_{n-1}|n\rangle. \quad (5.121)$$

Comparing the first and the last form of this equality, we see that $|A'_{n-1}| = n/|A_n| = n^{1/2}$, i.e. $A'_n = (n+1)^{1/2} \exp(i\varphi_n)$. Taking all phases φ_n and φ_n' equal to zero for simplicity, we may reduce Eqs. (115) to their final, standard form³³

$$\hat{a}^\dagger|n\rangle = (n+1)^{1/2}|n+1\rangle, \quad \hat{a}|n\rangle = n^{1/2}|n-1\rangle. \quad (5.122)$$

Up and
down the
Fock state
ladder

Now we can use these formulas to calculate, for example, the matrix elements of operator $\hat{x}$ in the Fock state basis:

$$\langle n'|\hat{x}|n\rangle = x_0 \langle n'|\hat{\xi}|n\rangle = \frac{x_0}{\sqrt{2}} \langle n'|\left(\hat{a} + \hat{a}^\dagger\right)|n\rangle = \frac{x_0}{\sqrt{2}} \left(\langle n'|\hat{a}|n\rangle + \langle n'|\hat{a}^\dagger|n\rangle \right). \quad (5.123)$$

To complete the calculation, we may now use Eqs. (122) and the Fock state orthonormality:

$$\langle n'|n\rangle = \delta_{n'n}. \quad (5.124)$$

The result is

$$\langle n'|\hat{x}|n\rangle = \frac{x_0}{\sqrt{2}} \left(n^{1/2} \delta_{n',n-1} + (n+1)^{1/2} \delta_{n',n+1} \right) = \left(\frac{\hbar}{2m\omega_0} \right)^{1/2} \left(n^{1/2} \delta_{n',n-1} + (n+1)^{1/2} \delta_{n',n+1} \right). \quad (5.125)$$

Coordinate's
matrix
elements

Acting absolutely similarly, for the momentum bra-kets we get a similar expression:

$$\langle n'|\hat{p}|n\rangle = i \left(\frac{\hbar m \omega_0}{2} \right)^{1/2} \left(-n^{1/2} \delta_{n',n-1} + (n+1)^{1/2} \delta_{n',n+1} \right) \quad (5.126)$$

Hence the matrices of both operators in the Fock-state basis have only two diagonals, adjacent to the main diagonal; all other elements (including the diagonal ones) are zeros.

³³ A useful mnemonic rule is that the c -number coefficient in any of these relations is equal to the square root of the *largest* number of the two states it relates.

Matrix elements of higher powers of these operators, as well as their products, may be handled similarly, though the higher is the power, the bulkier is the result. For example,³⁴

$$\begin{aligned}
 \langle n' | \hat{x}^2 | n \rangle &= \langle n' | \hat{x} \hat{x} | n \rangle = \sum_{n''=0}^{\infty} \langle n' | \hat{x} | n'' \rangle \langle n'' | \hat{x} | n \rangle \\
 &= \frac{x_0^2}{2} \sum_{n''=0}^{\infty} \left((n'')^{1/2} \delta_{n', n''-1} + (n''+1)^{1/2} \delta_{n', n''+1} \right) \left(n^{1/2} \delta_{n'', n-1} + (n+1)^{1/2} \delta_{n'', n+1} \right) \\
 &= \frac{x_0^2}{2} \left\{ [n(n-1)]^{1/2} \delta_{n', n-2} + [(n+1)(n+2)]^{1/2} \delta_{n', n+2} + (2n+1) \delta_{n', n} \right\}.
 \end{aligned} \tag{5.127}$$

For applications, the most important of these matrix elements are those on its main diagonal:

$$\langle x^2 \rangle = \langle n | \hat{x}^2 | n \rangle = \frac{x_0^2}{2} (2n+1). \tag{5.128}$$

This expression shows, in particular, that the expectation value of oscillator's potential energy in n -th Fock state is

$$\langle U \rangle = \frac{m\omega_0^2}{2} \langle x^2 \rangle = \frac{\hbar\omega_0}{2} \left(n + \frac{1}{2} \right). \tag{5.129}$$

This is exactly $\frac{1}{2}$ of the total energy (119) of the oscillator. As a sanity check, an absolutely similar calculation of the kinetic energy shows that

$$\left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2m} \langle n | \hat{p}^2 | n \rangle = \frac{\hbar\omega_0}{2} \left(n + \frac{1}{2} \right), \tag{5.130}$$

i.e. both partial energies equal $E_n/2$, just as in a classical oscillator.³⁵

5.5. The Glauber and squeezed states

There is evidently a huge difference between a quantum stationary (Fock) state of the oscillator and its classical state. Indeed, let us write the classical Hamilton equations of motion of the oscillator (using capital letters to distinguish the classical variables from arguments of quantum wavefunctions):

$$\dot{X} = \frac{P}{m}, \quad \dot{P} = -\frac{\partial U}{\partial X} = -m\omega_0^2 X. \tag{5.131}$$

On the “phase plane” with Cartesian coordinates x and p (Fig. 6), these equations describe clockwise rotation of the representation point $\{X(t), P(t)\}$ along an elliptic trajectory starting from the initial point $\{X(0), P(0)\}$. (The normalization of momentum by $m\omega_0$, similar to the one performed by the second of Eqs. (96), makes the trajectory pleasingly circular, with a constant radius equal to oscillation's amplitude A , reflecting the constant full energy

³⁴ The first line of Eq. (127), evidently valid for any time-independent system, is the simplest of the so-called *sum rules*, which will be repeatedly discussed below.

³⁵ Still note that operators of the partial (potential and kinetic) energies do *not* commute with either each other or with the full-energy (Hamiltonian) operator, so that the Fock states n are *not* their eigenstates.

$$E_c = \frac{m\omega_0^2}{2} A^2, \quad A^2 = [X(t)]^2 + \left[\frac{P(t)}{m\omega_0} \right]^2 = \text{const} = [X(0)]^2 + \left[\frac{P(0)}{m\omega_0} \right]^2, \quad (5.132)$$

determined by the initial conditions.)

For the forthcoming comparison with quantum states, it is convenient to describe this classical solution by the following dimensionless complex variable

$$\alpha(t) \equiv \frac{1}{\sqrt{2}x_0} \left(X(t) + i \frac{P(t)}{m\omega_0} \right), \quad (5.133)$$

which is essentially the standard complex-number representation of system's position on the 2D phase plane, with $|\alpha| \equiv A/\sqrt{2}x_0$. With this definition, Eqs. (131) are conveniently merged into one equation,

$$\dot{\alpha} = -i\omega_0\alpha, \quad (5.134)$$

with an evident, very simple solution

$$\alpha(t) = \alpha(0)e^{-i\omega_0 t}, \quad (5.135)$$

where the constant $\alpha(0)$ may be complex, and is just the (normalized) classical complex amplitude of oscillations.³⁶ This equation describes sinusoidal oscillations of both $X(t) \propto \text{Re}[\alpha(t)]$ and $P \propto \text{Im}[\alpha(t)]$, with a phase shift of $\pi/2$ between them.

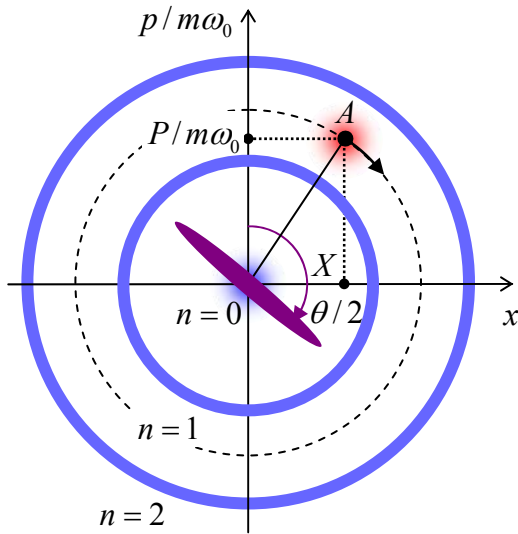


Fig. 5.6. Schematic representation of various states of a harmonic oscillator on the phase plane. The bold black point represents a classical state, with the dashed line showing its trajectory. (Very imperfect) classical images of the Fock states with $n = 0, 1$, and 2 are shown in blue, while the blurred red spot is the (equally schematic) Glauber state's image. Finally, the magenta elliptical spot is a classical image of a squeezed ground state. Arrows show the direction of states' evolution in time.

On the other hand, according to the basic Eqs. (4.157)-(4.158), the time dependence of a Fock state, as of a stationary state of the oscillator, is limited to the phase factor $\exp\{-iE_n t/\hbar\}$ not in observables, but rather in the wavefunction, and a result, gives time-independent expectation values of x , p , or of any function thereof. (Moreover, as Eqs. (125) and (126) show, $\langle x \rangle = \langle p \rangle = 0$.) Taking into

³⁶ See, e.g., CM Chapter 4, especially Eqs. (4.4) and Fig. 4.9 and its discussion.

account Eqs. (129) and (130), the closest (though very imperfect) geometric image³⁷ for such a state on the phase plane is a blurred circle of radius $A_n = x_0(2n + 1)^{1/2}$, along which the wavefunction is uniformly spread as a wave – see the blue rings in Fig. 6. For the ground state ($n = 0$), with wavefunction (2.269), a better image is a blurred round spot, of radius $\sim x_0$, at the origin.

However, the Fock states n are not the only possible quantum states of the oscillator: according to the basic Eq. (4.6), a state described by ket-vector

$$|\alpha\rangle = \sum_{n=0}^{\infty} \alpha_n |n\rangle \quad (5.136)$$

with any set of (complex) c -numbers α_n , is also its legitimate state, subject only to the normalization condition $\langle\alpha|\alpha\rangle = 1$, giving

$$\sum_{n=0}^{\infty} |\alpha_n|^2 = 1. \quad (5.137)$$

It is natural to ask: can we select coefficients α_n in such a special way that the state properties would be closer to the classical ones; in particular the expectation values $\langle x \rangle$ and $\langle p \rangle$ of coordinate and momentum would evolve in time just as the classical values $X(t)$ and $P(t)$, while the uncertainties of these observables would be time-independent and the same as in the ground state:

$$\delta x = \frac{x_0}{\sqrt{2}} = \left(\frac{\hbar}{2m\omega_0} \right)^{1/2}, \quad \delta p = \frac{m\omega_0 x_0}{\sqrt{2}} = \left(\frac{\hbar m\omega_0}{2} \right)^{1/2}, \quad (5.138)$$

with the smallest possible value of the uncertainty product, $\delta x \delta p = \hbar/2$.³⁸ Let me show that such a *Glauber state*,³⁹ which is schematically represented in Fig. 6 by a blurred red spot around the classical point $\{X(t), P(t)\}$, is indeed possible.

Conceptually the simplest way to find the corresponding coefficients α_n would be to calculate $\langle x \rangle$, $\langle p \rangle$, δx and δp for an arbitrary set of α_n , and then try to optimize these coefficients to reach our goal. However, this problem may be solved much easier using wave mechanics. Indeed, let us consider the following wavefunction

$$\Psi_\alpha(x, t) = C_0 \exp \left\{ -\frac{m\omega_0}{2\hbar} [x - X(t)]^2 + i \frac{P(t)x}{\hbar} \right\}. \quad (5.139)$$

Its comparison with Eqs. (2.16) and (2.269) shows that this is just a Gaussian wave packet with the average momentum P and the coordinate width δx given by Eq. (138), but shifted along axis x by X .

³⁷ I have to confess that such geometric mapping of a quantum state on the phase plane $[x, p]$ is not exactly defined; you may think about colored areas in Fig. 6 as regions of pairs $\{x, p\}$ most probably obtained in measurements. A quantitative definition of such a mapping will be given in Sec. 7.3 using the Wigner function, though, as we will see, even such imaging definition has certain internal contradictions. Still such cartoons may have considerable cognitive/heuristic value, if their limitations are kept in mind.

³⁸ In the quantum theory of measurements, Eqs. (138) are frequently referred to as the *standard quantum limit*.

³⁹ Named after R. J. Glauber who studied these states in detail in 1965, though they had been discussed in brief by E. Schrödinger as early as in 1926. Another popular name, “coherent”, for the Glauber states is very misleading, because all the quantum states we have studied so far (including the Fock states) may be presented as coherent (pure) superpositions of the basis states.

Hence, this wavefunction satisfies all the above requirements, and a straightforward (though a bit bulky) differentiation over x and t shows it also satisfies oscillator's Schrödinger equation, provided that that functions $X(t)$ and $P(t)$ satisfy classical Eqs. (131).

This fact is true even for a more general situation when the oscillator, initially in its ground state⁴⁰ comes under effect of a classical force $F(t)$. (Evidently, for its description it is sufficient to add this function to the right-hand part of the second of Eqs. (131).) Moreover, the electromagnetic radiation formed in “good” (single-mode) lasers is also in the Glauber state. (As will be discussed in Chapter 9, the experimental formation of Fock states n , with the only exception of $n = 0$, i.e. the ground state, is much harder.) This is why the Glauber states are so important.

Though Eq. (139) gives the full wave-mechanics description of a Glauber state, there is a substantial place for the bra-ket formalism here too. For example, in order to calculate the corresponding coefficients in expansion (136),

$$\alpha_n = \langle n | \alpha \rangle = \int dx \langle n | x \rangle \langle x | \alpha \rangle = \int \psi_n^*(x) \psi_\alpha(x) dx, \quad (5.140)$$

we would need to use not only the simple Eq. (139), but also the Fock state wavefunctions $\psi_n(x)$, which are not very appealing – see Eq. (2.279). Instead, this calculation may be readily done in the bra-ket formalism, giving us one important byproduct result.

Let us start from expressing the double shift of the ground state (by X and P), that has led us to Eq. (139), in the operator language. Forgetting about the P for a minute, let us find a *translation operator* $\hat{\tau}_X$ that produces the desirable shift of coordinate by X of an arbitrary wavefunction $\psi(x)$ – say represented as the standard wave packet (59). Evidently, the result of its action, in the coordinate representation, is

$$\hat{\tau}_X \psi(x) = \psi(x - X) = \frac{1}{(2\pi\hbar)^{1/2}} \int \varphi(p) \exp\left\{i \frac{p(x - X)}{\hbar}\right\} dp. \quad (5.141)$$

Hence, the shift may be achieved by the multiplication of each Fourier component of the packet, with momentum p , by $\exp\{-ipX/\hbar\}$. This gives us a hint that the general form of the translation operator, valid in *any* representation, should be

$$\hat{\tau}_X = \exp\left\{-i \frac{\hat{p}X}{\hbar}\right\}. \quad (5.142) \quad \text{X-translation operator}$$

The proof of this formula is provided by the fact that any operator is uniquely determined by the set of its matrix elements in any full and orthogonal basis, in particular the basis of momentum states p . According to Eq. (141), the analog of Eq. (23) for the p -representation, applied to the translation operator (which is evidently local), is

$$\langle p | \hat{\tau}_X | p' \rangle \varphi(p') = \delta(p - p') \exp\left\{-i \frac{pX}{\hbar}\right\} \varphi(p), \quad (5.143)$$

so that operator (142) does exactly the job we need it to.

⁴⁰ As will be discussed in Chapter 7, the ground state may be readily formed, for example, by providing a weak coupling of the oscillator to a low-temperature ($k_B T \ll \hbar \omega_0$) environment.

The operator that provides the shift of momentum by P is absolutely similar - with the opposite sign under the exponent, due to the opposite sign of the exponent in the reciprocal Fourier transform, so that the simultaneous shift by both X and P may be achieved by the following translation operator:

α -translation
operator

$$\hat{\tau}_\alpha = \exp\left\{i \frac{P\hat{x} - \hat{p}X}{\hbar}\right\}. \quad (5.144)$$

As we already know, for a harmonic oscillator the creation-annihilation operators are more natural, so that we may use Eqs. (96) and (99) to recast Eq. (144) as

$$\hat{\tau}_\alpha = \exp\left\{\alpha \hat{a}^\dagger - \alpha^* \hat{a}\right\}, \quad \text{with} \quad \hat{\tau}_\alpha^\dagger = \exp\left\{\alpha^* \hat{a} - \alpha \hat{a}^\dagger\right\}, \quad (5.145)$$

where the c -number α (generally, a function of time) is defined by Eq. (133). Now, according to Eq. (139), we may form the Glauber state's ket-vector just as

Glauber
state as
ground
state's
translation

$$|\alpha\rangle = \hat{\tau}_\alpha |0\rangle. \quad (5.146)$$

This formula looks nice and simple, but making practical calculations (say, calculating expectation values of variables) with the translation operator (144) is not too easy because of its exponent-of-operators form. Fortunately, it turns out that a much simpler representation for the Glauber state is possible. To show that, let us start with the following general (and very useful) property of exponential functions of operators: if

$$[\hat{A}, \hat{B}] = \mu \hat{I}, \quad (5.147)$$

(where $\hat{A}$ and $\hat{B}$ are arbitrary operators, and μ is a c -number), then⁴¹

$$\exp\left\{+\hat{A}\right\} \hat{B} \exp\left\{-\hat{A}\right\} = \hat{B} + \mu \hat{I}. \quad (5.148)$$

Let us apply Eqs. (147)-(148) to two cases, both with

$$\hat{A} = \alpha^* \hat{a} - \alpha \hat{a}^\dagger, \quad \text{so that} \quad \exp\left\{+\hat{A}\right\} = \hat{\tau}_\alpha^\dagger, \quad \exp\left\{-\hat{A}\right\} = \hat{\tau}_\alpha. \quad (5.149)$$

First, let us take $\hat{B} = \hat{I}$, then Eq. (147) is valid with $\mu = 0$, and Eq. (148) yields

$$\hat{\tau}_\alpha^\dagger \hat{\tau}_\alpha = \hat{I}, \quad (5.150)$$

This equality means that the translation operator is unitary – not a big surprise, because if we shift a classical point on the complex phase plane by $(+\alpha)$ and then by $(-\alpha)$, we certainly must come back to the initial position. Relation (150) means merely that this fact is also true for any quantum state as well.

Second, let us take $\hat{B} = \hat{a}$; in order to verify Eq. (147) and find the corresponding μ , let us calculate the commutator. Using, at the due stage of calculation, Eq. (104), we get

$$[\hat{A}, \hat{B}] = [\alpha^* \hat{a} - \alpha \hat{a}^\dagger, \hat{a}] = -\alpha [\hat{a}^\dagger, \hat{a}] = \alpha \hat{I}, \quad (5.151)$$

⁴¹ The proof of Eq. (148) may be readily achieved by expanding operator $\hat{f}(\lambda) \equiv \exp\left\{+\lambda \hat{A}\right\} \hat{B} \exp\left\{-\lambda \hat{A}\right\}$ in the Taylor series in the c -number parameter λ , and then evaluating the result at $\lambda = 1$.

so that in this case $\mu = \alpha$, and Eq. (148) yields

$$\hat{\tau}_\alpha^\dagger \hat{a} \hat{\tau}_\alpha = \hat{a} + \alpha \hat{I}. \quad (5.152)$$

We have approached the summit of this beautiful calculation. Let us consider operator

$$\hat{\tau}_\alpha \hat{\tau}_\alpha^\dagger \hat{a} \hat{\tau}_\alpha. \quad (5.153)$$

Using Eq. (150), we may reduce this expression to $\hat{a} \hat{\tau}_\alpha$, while the application of Eq. (151) to the same expression yields $\hat{\tau}_\alpha \hat{a} + \alpha \hat{\tau}_\alpha$. Hence, we get the following operator equality

$$\hat{a} \hat{\tau}_\alpha = \hat{\tau}_\alpha \hat{a} + \alpha \hat{\tau}_\alpha, \quad (5.154)$$

which may be applied to any state. Now acting by these two operators on the ground state $|0\rangle$ and using the facts that $\hat{a}|0\rangle$ is the null-state, while $\hat{\tau}_\alpha|0\rangle \equiv |\alpha\rangle$, we finally get a very simple and elegant result:⁴²

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle. \quad (5.155)$$

Glauber
state as
operator $\hat{a}$'s
eigenstate

Thus any Glauber state is just one of eigenstates of the annihilation operator, namely the one with the eigenvalue equal to parameter α , i.e. to the complex representation (133) of the classical state which is the center of the Glauber state's distribution.⁴³ This fact makes the calculations of the Glauber state properties much simpler. As the simplest example, let us use Eq. (155) to find $\langle x \rangle$ in the Glauber state:

$$\langle x \rangle = \langle \alpha | \hat{x} | \alpha \rangle = \frac{x_0}{\sqrt{2}} \langle \alpha | (\hat{a} + \hat{a}^\dagger) | \alpha \rangle = \frac{x_0}{\sqrt{2}} \left(\langle \alpha | \hat{a} | \alpha \rangle + \langle \alpha | \hat{a}^\dagger | \alpha \rangle \right). \quad (5.156)$$

In the first term in the parentheses, we can apply Eq. (155) directly, while in the second term, we can use the bra-counterpart of that relation, $\langle \alpha | \hat{a}^\dagger = \langle \alpha | \alpha^*$. Now assuming that the Glauber state is normalized, $\langle \alpha | \alpha \rangle = 1$, and using Eq. (133), we get

$$\langle x \rangle = \frac{x_0}{\sqrt{2}} \left(\langle \alpha | \alpha | \alpha \rangle + \langle \alpha | \alpha^* | \alpha \rangle \right) = \frac{x_0}{\sqrt{2}} (\alpha + \alpha^*) = X, \quad (5.157)$$

Acting absolutely similarly, we may readily extend this sanity check to verify that $\langle p \rangle = P$, and that δx and δp indeed obey Eq. (138).

As a more thorough sanity check, let us use Eq. (155) to re-calculate Glauber state's wavefunction (139). Inner-multiplying both sides of that relation by bra-vector $\langle x|$, and using definition (98a) of the annihilation operator, we get

⁴² It is also rather counter-intuitive. Indeed, according to Eq. (122), the annihilation operator $\hat{a}$, acting on a Fock state n , “beats it down” to the lower-energy state $(n - 1)$ – see Eq. (119). However, according to Eq. (155), its action on a Glauber state α does not lead to the state change and hence to an energy decrease! The resolution of this paradox may be achieved via representation of the Glauber state as a series of Fock states – see Eq. (165) below. Operator $\hat{a}$ indeed transfers each Fock component to a lower-energy state, but it also re-weighs each term of the expansion, so that the complete energy of the Glauber state remains constant.

⁴³ Note that the spectrum of eigenvalues α of eigenproblem (155) is continuous – it may be any complex number!

$$\frac{1}{\sqrt{2}x_0} \langle x | \left(\hat{x} + i \frac{\hat{p}}{m\omega_0} \right) | \alpha \rangle = \alpha \langle x | \alpha \rangle. \quad (5.158)$$

Since $\langle x |$ is the bra-vector of the eigenstate of the Hermitian operator $\hat{x}$, they may be swapped, with the operator giving its eigenvalue x ; acting on that bra-vector by the (local!) operator of momentum, we have to use it in the coordinate representation (63). As a result, we get

$$\frac{1}{\sqrt{2}x_0} \left(x \langle x | \alpha \rangle + \frac{\hbar}{m\omega_0} \frac{\partial}{\partial x} \langle x | \alpha \rangle \right) = \alpha \langle x | \alpha \rangle. \quad (5.159)$$

But $\langle x | \alpha \rangle$ is nothing else than the Glauber state's wavefunction Ψ_α , so that Eq. (153) gives for it a first-order differential equation

$$\frac{1}{\sqrt{2}x_0} \left(x \Psi_\alpha + \frac{\hbar}{m\omega_0} \frac{\partial}{\partial x} \Psi_\alpha \right) = \alpha \Psi_\alpha. \quad (5.160)$$

Chasing Ψ_α and x to the opposite sides of the equation, and using definition (133) of parameter α , we may bring this equation to a form

$$\frac{\partial \Psi_\alpha}{\Psi_\alpha} = \frac{m\omega_0}{\hbar} \left[-x + \left(X + i \frac{P}{m\omega_0} \right) \right] \partial x. \quad (5.161)$$

Integrating both parts, we return to Eq. (139) that had been derived by wave-mechanics means.

Now that we can use Eq. (155) for finding coefficients α_n in the expansion (136) of the Glauber state α in series over the Fock states n . Plugging Eq. (136) into each side of Eq. (155), using the first of Eq. (122) in the left-hand part, and requiring the coefficients at each ket-vector $|n\rangle$ in both parts to be equal, we get the following recurrence relation for the coefficients:

$$\alpha_{n+1} = \frac{\alpha}{(n+1)^{1/2}} \alpha_n. \quad (5.162)$$

Assuming some value of α_0 , and applying the relation sequentially for $n = 1, 2$, etc., we get

$$\alpha_n = \frac{\alpha^n}{(n!)^{1/2}} \alpha_0. \quad (5.163)$$

Now we can find α_0 from the normalization requirement (137), getting

$$|\alpha_0|^2 \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} = 1. \quad (5.164)$$

In this sum, we may readily recognize the Taylor expansion of function $\exp\{|\alpha|^2\}$, so that the final result (besides an arbitrary common phase multiplier) is

$$|\alpha\rangle = \exp\left\{-\frac{|\alpha|^2}{2}\right\} \sum_{n=0}^{\infty} \frac{\alpha^n}{(n!)^{1/2}} |n\rangle. \quad (5.165)$$

Glauber
state as
Fock states'
superposition

It means in particular that the probability $W_n \equiv \alpha_n \alpha_n^*$ of finding the system energy on n -th energy level (119) obeys the well-known Poisson distribution (Fig. 7):

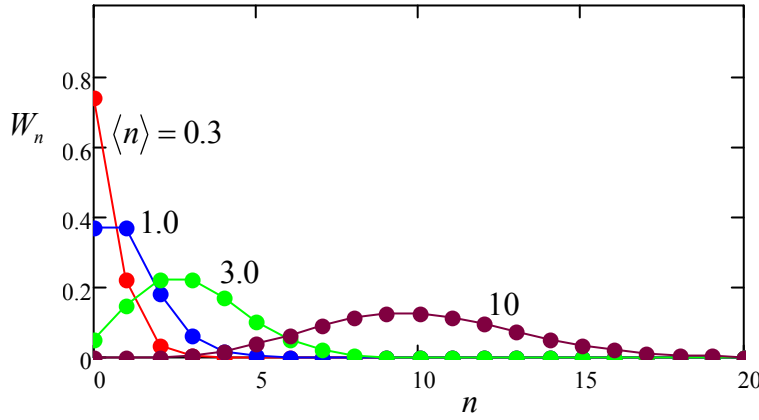


Fig. 5.7. The Poisson distribution for several values of $\langle n \rangle$. Note that W_n are defined only for integer values of n ; lines are only guides for the eye.

$$W_n = \frac{\langle n \rangle^n}{n!} e^{-\langle n \rangle},$$

(5.166) Poisson distribution

where in our particular case

$$\langle n \rangle = |\alpha|^2. \quad (5.167)$$

For applications, perhaps the most important mathematical property of this distribution is

$$\delta n = \langle n \rangle^{1/2};$$

(5.168) r.m.s. fluctuation

note also that at $\langle n \rangle \gg 1$, and hence $\delta n \ll \langle n \rangle$, the Poisson distribution approaches the Gaussian (“normal”) one.

Now let us discuss the evolution of the Glauber state in time. In the Schrödinger language, it is completely described by dynamics (131) of the c -number shifts $X(t)$ and $P(t)$ participating in wavefunction (139). Note again that, in contrast to the spread of the wave packet of a free particle, discussed in Sec. 2.2, in the harmonic oscillator the Gaussian packet of special width (138) does not spread at all!

An alternative and equivalent way of dynamics description is to use the Heisenberg equation of motion. As Eqs. (42) and (48) tell us, such equations for Heisenberg operators of coordinate and momentum they have to be similar to the classical equation (131):

$$\dot{\hat{x}}_H = \frac{\hat{p}_H}{m}, \quad \dot{\hat{p}}_H = -m\omega_0^2 \hat{x}_H. \quad (5.169)$$

Now using Eqs. (98), for the Heisenberg-picture creation and annihilation operators we get equations

$$\dot{\hat{a}}_H = -i\omega_0 \hat{a}_H, \quad \dot{\hat{a}}_H^\dagger = +i\omega_0 \hat{a}_H^\dagger, \quad (5.170)$$

that are completely similar for the classical equation (134) for the c -number parameter α and its complex conjugate, and hence have the solutions identical to Eq. (135):

$$\hat{a}_H(t) = \hat{a}_H(0)e^{-i\omega_0 t}, \quad \hat{a}_H^\dagger(t) = \hat{a}_H^\dagger(0)e^{i\omega_0 t}. \quad (5.171)$$

As was discussed in Sec. 4.6, such equations are very convenient because they enable simple calculation of time evolution of observables for any initial state of the oscillator (Fock, Glauber, or any other) using Eq. (4.191). Applied to a Glauber state $\alpha(0)$, such calculation gives the same results as have already been derived earlier in this section, in particular confirms that the Gaussian wave packet of the special width (138) does not spread in time.

Now let us consider what happens if the initial wave packet is still Gaussian, but has a different width, say $\delta x < x_0/\sqrt{2}$. As we already know from Sec. 2.2, the momentum spread δp will be correspondingly larger, still with the smallest uncertainty product: $\delta x \delta p = \hbar/2$. Such *squeezed ground state* ψ , with zero expectation values of x and p , may be generated from the Fock/Glauber ground state:

Squeezed
ground
state

$$|\psi\rangle = \hat{\mathcal{S}}_\psi |0\rangle, \quad (5.172a)$$

using the so-called *squeezing operator*,

Squeezing
operator

$$\hat{\mathcal{S}}_\psi = \exp\left\{\frac{1}{2}\left(\psi^* \hat{a}\hat{a} - \psi \hat{a}^\dagger \hat{a}^\dagger\right)\right\}, \quad (5.172b)$$

which depends on a complex c -number parameter $\psi = re^{i\theta}$. Parameter's modulus r determines the squeezing degree; it is straightforward to use Eq. (172) for checking that if ψ is real ($\theta = 0$, $\xi = r$), then

$$\delta x = \frac{x_0}{\sqrt{2}} e^{-r} = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} e^{-r}, \quad \delta p = \frac{m\omega_0 x_0}{\sqrt{2}} e^r = \left(\frac{\hbar m\omega_0}{2}\right)^{1/2} e^r, \quad \text{so that } \delta x \delta p = \frac{\hbar}{2}. \quad (5.173)$$

On the phase plane (Fig. 6), this state, with $r > 0$, may be represented by an oval spot squeezed along axis x (hence the state's name) and stretched along axis p ; the same formulas but with $r < 0$ describe the opposite squeezing. On the other hand, phase θ of the squeeze parameter ψ determines the angle $\theta/2$ of oval's turn about the phase plane origin – see the magenta ellipse in Fig. 6; if $\theta \neq 0$, Eqs. (173) are valid for variables $\{x', p'\}$ obtained from $\{x, p\}$ via clockwise rotation by that angle. For any of such origin-centered squeezed states, time evolution is reduced to an increase of the angle with rate ω_0 , i.e. to the clockwise rotation of the ellipse, without its deformation, with angular velocity ω_0 – see the magenta arrows in Fig. 6. As a result, uncertainties δx and δp oscillate in time with double frequency $2\omega_0$, while their product is constant at its minimal possible value $\hbar/2$.

Such squeezed ground states have important implications for quantum measurements (see Sec. 7.7 below) and may be formed, for example, by parametric excitation of the oscillator,⁴⁴ with a parameter modulation depth close to, but still below the threshold of parametric oscillations excitation. Unfortunately, I do have time for a further discussion of this interesting topic,⁴⁵ but still need to mention

⁴⁴ For a discussion and classical theory of this effect, see, e.g., CM Sec. 4.5.

⁴⁵ See, e.g., Chapter 7 in C. Gerry and P. Knight, *Introductory Quantum Optics*, Cambridge U. Press, 2005, and the spectacular measurements of the Glauber and squeezed states of electromagnetic (light) oscillators by G. Breitenbach *et al.*, *Nature* **387**, 471 (1997), very large (ten-fold) squeezing in such oscillators by H. Vahlbruch *et al.*, *Phys. Rev. Lett.* **100**, 033602 (2008); and recent first measurements of the (so far, slight) squeezing in mechanical resonators, with eigenfrequency $\omega_0/2\pi$ as low as 3.6 MHz, by E. Wollman *et al.*, *Science* **349**, 952 (2015).

a more general class of squeezed states, centered to an *arbitrary* point $\{X, P\}$ rather than the origin, that may be formed by an additional action of the displacement operator (144) on the squeezed ground state (172). Calculations similar to those that led us from Eq. (145) to Eq. (155), but now for the product operator $\hat{\mathcal{T}}_\alpha \hat{\mathcal{S}}_s$ rather than bare $\hat{\mathcal{T}}_\alpha$, show that such a general squeezed state is an eigenstate of the following mixed operator

$$\hat{b} \equiv \hat{a} \cosh r + \hat{a}^\dagger e^{i\theta} \sinh r, \quad (5.174a)$$

with eigenvalue

$$\beta = \alpha \cosh r + \alpha^* e^{i\theta} \sinh r. \quad (5.174b)$$

For the particular case $\alpha = 0$, Eq. (174b) yields $\beta = 0$, i.e. the action of operator (174a) on the squeezed ground state ψ with the same r and θ yields the null-state, thus generalizing Eq. (118), which is valid for the “usual” (non-squeezed) ground state.

5.6. Revisiting spherically-symmetric problems

One more blank spot to fill has been left in our study of wave mechanics of spherically-3D symmetric systems in Sec. 3.6. Indeed, while the eigenfunctions describing axially-symmetric 2D systems, and the azimuthal components of those in spherically-symmetric 3D systems, are very simple,

$$\psi_m = \frac{1}{(2\pi)^{1/2}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots \quad (5.175)$$

the polar components of the eigenfunctions in the latter case (i.e., of spherical harmonics) include the associate Legendre functions $P_l^m(\cos\theta)$ that may be expressed via elementary functions only indirectly – see Eqs. (3.165) and (3.168). This makes all the calculations less than transparent and, in particular, does not allow a clear insight into the origin of the very simple eigenvalue spectrum – see, e.g., Eq. (3.163). The bra-ket formalism, applied to the angular momentum operator, allows one to get such insight, and also produces a very convenient tool for many calculations involving spherically-symmetric potentials.

Let us start from using the correspondence principle to spell out the quantum-mechanical operator of the orbital angular momentum $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$ of a point particle:

$$\hat{\mathbf{L}} \equiv \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \begin{vmatrix} \mathbf{n}_x & \mathbf{n}_y & \mathbf{n}_z \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}, \quad \text{i.e. } \hat{L}_x \equiv \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \text{etc.}, \quad (5.176)$$

Angular momentum operator

From this definition, we can readily calculate the commutation relations for all Cartesian components of operators $\hat{\mathbf{L}}$, $\hat{\mathbf{r}}$, and $\hat{\mathbf{p}}$; for example,

$$[\hat{L}_x, \hat{y}] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{y}] = -\hat{z}[\hat{p}_y, \hat{y}] = i\hbar\hat{z}, \quad (5.177)$$

etc. Using the sequential numbering of coordinate axes ($x = r_1$, etc.), the summary of these calculations may be presented in similar, compact (and beautiful!) forms:

Key
commutation
relations

$$[\hat{L}_j, \hat{r}_{j'}] = i\hbar \hat{r}_{j''} \varepsilon_{jj'j''}, \quad [\hat{L}_j, \hat{p}_{j'}] = i\hbar \hat{p}_{j''} \varepsilon_{jj'j''}, \quad [\hat{L}_j, \hat{L}_{j'}] = i\hbar \hat{L}_{j''} \varepsilon_{jj'j''}, \quad (5.178)$$

where each of indices j and j' and j'' may take any of values 1, 2, and 3, j'' is the complementary index of the same set (not equal to either j or j'), and $\varepsilon_{jj'j''}$ is the Levi-Civita symbol (or “permutation symbol”).⁴⁶ Also introducing in the natural way a (scalar!) operator of the observable $L^2 = |\mathbf{L}|^2$,

Operator
of L^2

$$\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \quad (5.179)$$

it is straightforward to check that this operator commutes with each of the Cartesian components:

$$[\hat{L}^2, \hat{L}_j] = 0. \quad (5.180)$$

This result, at the first sight, may seem to contradict the last of Eqs. (178). Indeed, haven't we learned in Sec. 4.5 that commuting operators (e.g., $\hat{L}^2$ and any of $\hat{L}_j$) share their eigenstate sets? If yes, shouldn't that mean that this set has to be common for all 4 operators?⁴⁷ The resolution in this paradox may be found in the condition that was mentioned just after Eq. (4.138), but (sorry!) not sufficiently emphasized there. According to that relation, if an operator has *degenerate* eigenstates (i.e. if $A_j = A_{j'}$ even for $j \neq j'$), they should not be necessarily shared by another compatible operator. This is exactly the situation with the orbital angular momentum operators, that may be schematically shown at a *Venn diagram* (Fig. 8):⁴⁸ the set of eigenstates of operator $\hat{L}^2$ is highly degenerate,⁴⁹ and is broader than those of the component operators $\hat{L}_j$ (that, as will be shown below, are non-degenerate until we consider particle's spin).

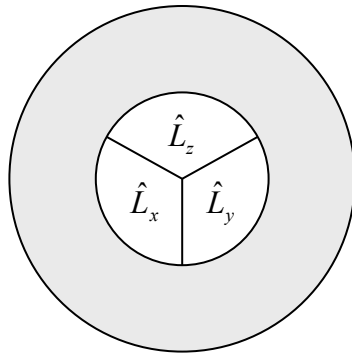


Fig. 5.8. Venn diagram showing (schematically) the partitioning of the set of eigenstates of operator $\hat{L}^2$. Each inner sector corresponds to the states shared with one of Cartesian component operators $\hat{L}_j$, while the outer (shaded) ring presents the eigenstates of $\hat{L}^2$ that are not shared with either of $\hat{L}_j$ - e.g., all linear combinations of eigenstates of different component operators.

⁴⁶ See, e.g., MA Eq. (13.2).

⁴⁷ The importance of this issue stems from the following fact: it is easy (and is hence left to the reader :-)) to use Eqs. (5.178) to prove that operators of all L_j and of L^2 commute with the Hamiltonian of a particle in the spherically-symmetric potential $U(r)$, and hence all their eigenstates are the stationary states in such a field.

⁴⁸ This is just a particular example of *Venn diagrams* (introduced in the 1880s by J. Venn) that show possible relations (such as intersections, unions, complements, etc.) between various sets of objects, and are a very useful tool in the general set theory.

⁴⁹ Note that this particular result is consistent with the classical picture of the angular momentum vector: even when its length is fixed, the vector may be oriented in various directions, corresponding to different values of its Cartesian components. However, in the classical picture, all these components may be fixed simultaneously, while in the quantum picture this is not true.

Let us focus on just one of these 3 joint sets of eigenstates – by tradition, of operators $\hat{L}^2$ and $\hat{L}_z$. (This tradition is due to the canonical form of spherical coordinates, in which the polar angle is measured from axis z . Indeed, using Eqs. (63), in the coordinate representation we get the following expression,

$$\hat{L}_z \equiv \hat{x}p_y - \hat{y}p_x = x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\varphi}. \quad (5.181)$$

Writing the standard eigenproblem for the operator in this representation, $\hat{L}_z\psi_m = L_z\psi_m$, we see that it is satisfied by eigenfunctions (175), with eigenvalues $L_z = \hbar m$ - at was already conjectured in Sec. 3.5.) More specifically, let us consider a set of eigenstates $\{|l, m\rangle\}$ corresponding to a certain degenerate eigenvalue of operator $\hat{L}^2$ but all possible eigenvalues of operator $\hat{L}_z$, i.e. all possible quantum numbers m . (At this point, l is just some parameter that determines the eigenvalue of $\hat{L}^2$; it will be defined more explicitly in a minute.) In order to analyze this set, it is instrumental to introduce the so-called *ladder* (also called, respectively, “raising” and “lowering”) operators

$$\hat{L}_{\pm} \equiv \hat{L}_x \pm i\hat{L}_y \quad (5.182)$$

Ladder operators and main commutation relations

- note a substantial similarity between this definition and Eqs. (98). It is straightforward to use this definition and the last of Eqs. (178) to calculate the following commutators:

$$[\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z, \quad \text{and} \quad [\hat{L}_z, \hat{L}_{\pm}] = \pm\hbar\hat{L}_{\pm}, \quad (5.183)$$

and use Eq. (179) to prove another important relation:

$$\hat{L}^2 = \hbar\hat{L}_z + \hat{L}_-^2 + \hat{L}_+^2. \quad (5.184)$$

Important commutation relations

Now let us rewrite the last of Eqs. (183) as

$$\hat{L}_z\hat{L}_{\pm} = \hat{L}_{\pm}\hat{L}_z \pm \hbar\hat{L}_{\pm}, \quad (5.185)$$

and act by its both parts on the ket-vector $|l, m\rangle$ of the set specified above:

$$\hat{L}_z\hat{L}_{\pm}|l, m\rangle = \hat{L}_{\pm}\hat{L}_z|l, m\rangle \pm \hbar\hat{L}_{\pm}|l, m\rangle. \quad (5.186)$$

Since eigenvalues of operator $\hat{L}_z$ are equal to $\hbar m$, in the first term of the right-hand part we may write

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle. \quad (5.187)$$

With that, Eq. (186) may be recast as

$$\hat{L}_z(\hat{L}_{\pm}|l, m\rangle) = \hbar(m \pm 1)(\hat{L}_{\pm}|l, m\rangle) \quad (5.188)$$

In a spectacular similarity with Eqs. (111)-(112) for the harmonic oscillator, Eq. (188) means that states $\hat{L}_{\pm}|l, m\rangle$ are also the eigenstates of operator $\hat{L}_z$, corresponding to eigenvalues $(m \pm 1)$. Thus the ladder operators act exactly as the creation and annihilation operators in the oscillator, moving the system up or down a ladder of eigenstates (Fig. 9). The most significant difference is that now the state

ladder must end in both directions, because an infinite increase of $|m|$, with whatever sign, would cause the expectation values of operator

$$\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2, \quad (5.189)$$

which corresponds to a non-negative observable, to become negative. Hence there should be two states on both ends of the ladder, $|l, m_{\max}\rangle$ and $|l, m_{\min}\rangle$, for whom

$$\hat{L}_+ |l, m_{\max}\rangle = 0, \quad \hat{L}_- |l, m_{\min}\rangle = 0. \quad (5.190)$$

Due to the symmetry of the whole problem with respect to the replacement $m \rightarrow -m$, we should have $m_{\min} = -m_{\max}$. This $m_{\max}$ is exactly the quantum number that is traditionally called l , so that

$$-l \leq m \leq +l. \quad (5.191)$$

Relation
between
 m and l

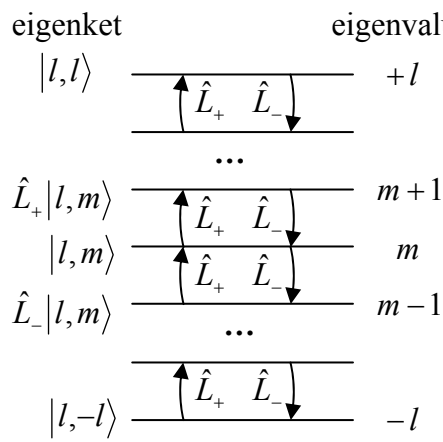


Fig. 5.9. Hierarchy (ladder diagram) of the common eigenstates of operators $\hat{L}^2$ and $\hat{L}_z$.

Evidently, this relation of quantum numbers m and l is compatible with the almost-classical image of various orientations of the angular momentum vector of the same length in various directions, with its z -component taking several $(2l + 1)$ possible values $\hbar m$. In this simple picture, however, L^2 would be equal to square of $(L_z)_{\max}$, i.e. to $(\hbar l)^2$; however, this is not so. Indeed, applying the operator equality (184) to the top state $|l, m_{\max}\rangle \equiv |l, l\rangle$, we get

$$\begin{aligned} \hat{L}^2 |l, l\rangle &= \hbar \hat{L}_z |l, l\rangle + \hat{L}_z^2 |l, l\rangle + \hat{L}_- \hat{L}_+ |l, l\rangle = \hbar^2 l |l, l\rangle + \hbar^2 l^2 |l, l\rangle + 0 \\ &= \hbar^2 l(l+1) |l, l\rangle. \end{aligned} \quad (5.192)$$

Eigenvalues
of L^2

Since by our initial assumption, all eigenvectors $|l, m\rangle$ correspond to the same eigenvalue of operator $\hat{L}^2$, this result means that all these eigenvalues are equal to $\hbar^2 l(l+1)$. Just as in case of the spin- $1/2$ vector operators, the deviation of this result from $\hbar^2 l^2$ may be interpreted as the result of unavoidable uncertainties (“fluctuations”) of the x - and y -components of the angular momentum, that give a finite positive contribution to L^2 even if the angular momentum vector is aligned in the best possible way with the z -axis.

Now let us compare our results with those of Sec. 3.6. Using the expression of Cartesian coordinates via the spherical ones exactly as was done in Eq. (181), we get the following expressions for the ladder operators (182) in the coordinate representation:

$$\hat{L}_{\pm} = \hbar e^{\pm i\varphi} \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right). \quad (5.193)$$

Coordinate
representation
of angular
momentum
operators

Now plugging this equation, together with Eq. (181), into Eq. (184), we get

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]. \quad (5.194)$$

But this is exactly the operator (besides its division by constant parameter $2mR$) that stands in the left-hand part of Eq. (3.156). Hence that equation, which was explored by the “brute-force” (wave-mechanical) approach in Sec. 3.6, may be understood as the eigenproblem for operator $\hat{L}^2$ in the coordinate representation, with eigenfunctions $Y_l^m(\theta, \varphi)$ corresponding to eigenkets $\{|l, m\rangle\}$, and eigenvalues $L^2 = 2mRE$. As a reminder, the main result of that, rather involved analysis was expressed by Eq. (3.163), which now may be rewritten as

$$L_l^2 = 2mR^2 E_l = \hbar^2 l(l+1), \quad (5.195)$$

in a full agreement with what was obtained in this section by much more efficient means based on the bra-ket formalism. In particular, it is fascinating to see how easy are now many operations with eigenvectors $|l, m\rangle$, albeit wavefunctions of these states, spherical harmonics $Y_l^m(\theta, \varphi)$, have rather complex spatial behavior – please have one more look at Eq. (3.171) and Fig. 3.19.⁵⁰

5.7. Spin and its addition to orbital angular momentum

Surprisingly, the theory described in the last section is useful for much more than orbital motion analysis. In particular, it helps to generalize the spin- $\frac{1}{2}$ results discussed in Chapter 4 to other values of spin s – the parameter still has to be defined. For that, let us notice that the commutation relations that were derived, for $s = \frac{1}{2}$, from the Pauli matrix properties, may be rewritten in exactly the same form as Eqs. (178) and (180) for the orbital momentum:

$$[\hat{S}_j, \hat{S}_{j'}] = i\hbar \hat{S}_{j''} \epsilon_{jjj''}, \quad [\hat{S}^2, \hat{S}_j] = 0. \quad (5.196)$$

Spin
operators:
commutation
relations

It has been postulated (and confirmed by numerous experiments) that these relations hold true for any quantum particle. Now note that all the calculations of the last section have been based *almost* exclusively on such relations – the exception will be discussed imminently. Hence, we may repeat them for spin operators, and get the relations similar to Eq. (187) and (192):

⁵⁰ The reader is challenged to use the commutation relations discussed above to prove one more important property of the common eigenstates of operators $\hat{L}_z$ and $\hat{L}^2$:

$$\langle l, m | \hat{r}_j | l', m' \rangle = 0, \quad \text{if either } l' \neq l \pm 1, \text{ or } m \neq m', \text{ or both.}$$

This property is the basis of the *selection rules* for dipole quantum transitions, to be discussed later in the course, especially in Sec. 9.3.

Spin
operators:
eigenstates
and
eigenvalues

$$\hat{S}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle, \quad \hat{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle, \quad 0 \leq s, \quad -s \leq m_s \leq +s, \quad (5.197)$$

where m_s is a quantum number similar to the orbital number m , and the non-negative constant s is defined as the maximum value of $|m_s|$. This parameter is exactly what is called *particle's spin* - in the narrow sense of the word.

Now let us return to the only part of our orbital moment calculations that has *not* been derived from the commutation relations. This was the fact, based on solution (175) of the orbital motion problems, that quantum numbers m (the analog of m_s) are integer. For spin, we do not have such a solution, so that the spectrum of numbers m_s (and hence its limits $\pm s$) should be found from the more loose requirement that the eigenstate ladder, extending from $-s$ to $+s$, has an integer number of steps. Hence, $2s$ has to be integer, i.e. spin s of a quantum particle may be either *integer* (as it is, for example, for photons and gluons), or *half-integer* (e.g., for all quarks and leptons including electrons).⁵¹

For $s = 1/2$, this picture yields all spin properties of electron that were derived in Chapter 4 from postulate (4.117). In particular, operators $\hat{S}^2$ and $\hat{S}_z$ have only 2 common eigenstates, with $S_z = \hbar m_s = \pm \hbar/2$, and both with $S^2 = s(s+1)\hbar^2 = (3/4)\hbar^2$. Note that this analogy with the angular momentum sheds a new light on the symmetry properties of electrons. Indeed, the fact that m in Eq. (175) is integer was derived in Sec. 3.5 from the requirement that making a full circle around axis z , we should find a similar value of wavefunction ψ_m , which differs from the initial one by an inconsequential factor $\exp\{2\pi i m\}$. With the replacement $m \rightarrow m_s = \pm 1/2$, such operation would multiply the wavefunction by $\exp\{\pm \pi i\}$, i.e. reverse its sign. On course, spin cannot be described by a usual wavefunction, but this *odd parity* of electrons (and all other spin- $1/2$ particles) is clearly revealed in multiparticle systems – see Chapter 8.

Now we are sufficiently equipped to analyze particles that have both the orbital momentum and the spin. In classical mechanics, such a particle would be characterized by the *total angular momentum* vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Following the correspondence principle, we may make an assumption that quantum-mechanical properties of this observable may be analyzed using the similarly defined vector operator:

Total
angular
momentum
operator

$$\hat{\mathbf{J}} \equiv \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (5.198)$$

with Cartesian components

$$\hat{J}_z \equiv \hat{L}_z + \hat{S}_z, \quad (5.199)$$

etc, and the magnitude squared equal to

$$\hat{J}^2 \equiv \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2. \quad (5.200)$$

Let us examine the properties of this vector operator. Since its two components describe different degrees of freedom of the particle (again, you may say “belong to different Hilbert spaces”), they may be considered as completely commuting:

$$[\hat{L}_j, \hat{S}_{j'}] = 0, \quad [\hat{L}^2, \hat{S}^2] = 0. \quad (5.201)$$

⁵¹ As a reminder, in the Standard Model of particle physics, such hadrons as mesons and baryons (notably including protons and neutrons) are essentially composite particles, with the spin equal to the sum of its component quark spins. However, at nonrelativistic energies, protons and neutrons may be considered fundamental particles with $s = 1/2$.

These above equalities are sufficient to derive the commutation rules of the total angular momentum, and, not surprisingly, they turn out to be absolutely similar to those of its components:

$$[\hat{J}_j, \hat{J}_{j'}] = i\hbar \hat{J}_{j''} \epsilon_{jjj''}, \quad [\hat{J}^2, \hat{J}_j] = 0. \quad (5.202)$$

Total
momentum:
commutation
relations

Now repeating all arguments of the last section, we may derive the following expressions for the common eigenstates of operators $\hat{J}^2$ and $\hat{J}_z$:

$$\hat{J}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle, \quad \hat{J}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle, \quad 0 \leq j, \quad -j \leq m_j \leq +j, \quad (5.203)$$

Total
momentum:
eigenstates,
and
eigenvalues

where j and m_j are new quantum numbers. Repeating the arguments made for m_s , we may conclude that j and m_j may be either integer or half-integer.

Before we proceed, one remark on notation: it is very convenient to use the same letter m for numbering eigenstates of all momentum components participating in Eq. (199), with corresponding indices (j , l , and s), in particular, to replace what we called m with m_l . With this replacement, the main results of the last section may be summarized in the form similar to Eqs. (197) and (203):

$$\hat{L}_z |l, m_l\rangle = \hbar m_l |l, m_l\rangle, \quad \hat{L}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle, \quad 0 \leq l, \quad -l \leq m_l \leq +l. \quad (5.204)$$

In order to understand which eigenstates used in Eqs. (197), (203), and (204) are compatible with each other, let us use Eqs. (198)-(202) to calculate the mutual commutators of the operators squared and their z -components. The result is

$$[\hat{J}^2, \hat{L}^2] = 0, \quad [\hat{J}^2, \hat{S}^2] = 0, \quad (5.205)$$

$$[\hat{J}^2, \hat{L}_z] \neq 0, \quad [\hat{J}^2, \hat{S}_z] \neq 0. \quad (5.206)$$

This result may be presented schematically on the following Venn diagram (Fig. 10), in which the crossed arrows indicate the only *non*-commuting pairs of operators.

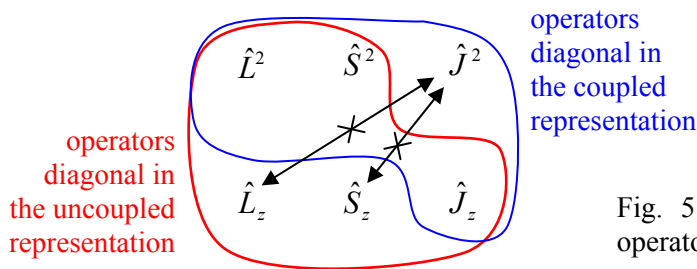


Fig. 5.10. Venn diagram for angular momentum operators, and their mutually-commuting groups.

This means that just as for each component angular momentum (**J**, **L**, and **S**) considered separately we could select a group of common eigenstates for its magnitude squared and the z -component, we also may find eigenstates shared by two broader groups of operators, encircled with colored lines in Fig. 10. The first group (within the red circle), consists of all operators but $\hat{J}^2$. This means that there are eigenstates shared by 5 remaining operators, and they may be characterized by certain values of the corresponding quantum numbers: l , m_l , s , m_s , and m_j . Actually, only 4 of these

numbers are independent, because due to Eq. (199) for these compatible operators, for each eigenstate of the group, their “magnetic” quantum numbers m have to satisfy the following relation:

$$m_j = m_l + m_s. \quad (5.207)$$

Hence the common eigenstates of the operators of this group are fully defined by just 4 quantum numbers, for example, l , m_l , s , and m_s . For some calculations, especially those for systems whose Hamiltonians include only operators of this group, it is convenient to use this set of eigenstates as the basis; frequently this is called the *uncoupled representation*.

However, in some situations we cannot ignore interactions between the orbital and spin degrees of freedom (in the common jargon, the *spin-orbit coupling*), which leads in particular to splitting (called the *fine structure*) of atomic energy levels even in the absence of external magnetic field. I will discuss these effects in detail in the next chapter, and now will only note that they may be described by a separate term, proportional to product $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, in the system's Hamiltonian. If this term is not negligible, the uncoupled representation becomes inconvenient. Indeed, writing

$$\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (5.208)$$

and looking at Fig. 10 again, we see that the operator $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, describing the spin-orbit coupling, does not commute with operators $\hat{L}_z$ and $\hat{S}_z$. This means that stationary states of the system with such term in the Hamiltonian do not belong to the uncoupled representation basis. On the other hand, Eq. (208) shows that operator $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ does commute with all 4 operators of another group, encircled with the blue line in Fig. 10. According to Eqs. (201), (202), and (205), all operators of that group also commute to each other, so that they have common eigenstates that may be marked by the corresponding quantum numbers, l , s , j , and m_j . This group is the basis for the *coupled representation* of particle's state.

Excluding the quantum numbers l and s , common for both groups, from notation, it is convenient to denote the common ket-vectors of each group as, respectively,

Coupled and
uncoupled
bases

$$\begin{aligned} |m_l, m_s\rangle, & \text{ for the uncoupled representation's basis,} \\ |j, m_j\rangle, & \text{ for the coupled representation's basis.} \end{aligned} \quad (5.209)$$

As we will see in the next chapter, for solution of some important problems (e.g., the fine structure of atomic spectra and the Zeeman effect), we will need the relation between the kets $|j, m_j\rangle$ and the kets $|m_l, m_s\rangle$. This relation may be represented as the usual linear superposition,

Definition of
Clebsch-
Jordan
coefficients

$$|j, m_j\rangle = \sum_{m_l, m_s} |m_l, m_s\rangle \langle m_l, m_s | j, m_j \rangle, \quad (5.210)$$

whose bra-kets (c -numbers), essentially the elements of the unitary matrix of the transformation between two eigenstate bases (209), are called the *Clebsch-Gordan coefficients*.

The best (though imperfect) classical interpretation of Eq. (210) I can offer is as follows. If the lengths of vectors $\mathbf{L}$ and $\mathbf{S}$ (in quantum mechanics associated with numbers l and s , respectively), and also their scalar product $\mathbf{L} \cdot \mathbf{S}$, are all fixed, then so is the length of vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (whose length in quantum mechanics is described by quantum number j). Hence, the classical image of a specific eigenket $|j, m_j\rangle$, in which l , s , j , and m_j are all fixed, is a state in which L^2 , S^2 , J^2 , and J_z are fixed.

However, this fixation still allows for an arbitrary rotation of the pair of vectors $\mathbf{L}$ and $\mathbf{S}$ (with a fixed angle between them, and hence fixed $\mathbf{L} \cdot \mathbf{S}$ and J^2) about the direction of vector $\mathbf{J}$ - see Fig. 11.

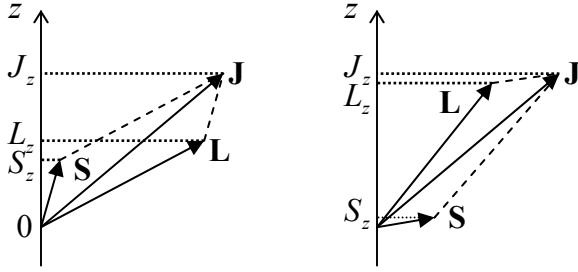


Fig. 5.11. Classical image of two quantum states with the same l, s, j , and m_j , but different m_l and m_s .

Hence the components L_z and S_z in these conditions are *not* fixed, and in classical mechanics may take a continuum of values, two of which (with the largest and smallest possible values of S_z) are shown in Fig. 11. In quantum mechanics, these components are quantized, with their states represented by eigenkets $|m_l, m_s\rangle$, so that a linear combination of such kets is necessary to represent ket $|j, m_j\rangle$. This is exactly what Eq. (210) does.

Some of properties of the Clebsch-Gordan coefficients $\langle m_l, m_s | j, m_j \rangle$ may be readily established. For example, the coefficients do not vanish only if the involved magnetic quantum numbers satisfy Eq. (207); let us prove this fact.⁵² All matrix elements of the null-operator

$$\hat{J}_z - (\hat{L}_z + \hat{S}_z) = \hat{0} \quad (5.211)$$

should equal zero in any basis; in particular

$$\langle j, m_j | \hat{J}_z - (\hat{L}_z + \hat{S}_z) | m_l, m_s \rangle = 0. \quad (5.212)$$

Acting by operator $\hat{J}_z$ on the bra-vector, and by the sum $(\hat{L}_z + \hat{S}_z)$ on the ket-vector, we get

$$[m_j - (m_l + m_s)] \langle j, m_j | m_l, m_s \rangle = 0, \quad (5.213)$$

thus proving that $\langle m_l, m_s | j, m_j \rangle \equiv \langle j, m_j | m_l, m_s \rangle^* = 0$, if $m_j - (m_l + m_s) \neq 0$.

For the most important case of spin- $\frac{1}{2}$ particles ($s = \frac{1}{2}$, and hence $m_s = \pm \frac{1}{2}$), whose uncoupled representation basis includes $2 \times (2l + 1)$ states, restriction (207) enables the representation of all nonvanishing Clebsch-Gordan coefficients on the simple diagram shown in Fig. 12. Indeed, each coupled-representation eigenket $|j, m_j\rangle$, with $m_j = m_l + m_s = m_l \pm \frac{1}{2}$, may be related with non-zero Clebsch-Gordan coefficients to at most two uncoupled-representation eigenstates $|m_l, m_s\rangle$. Since m_l may only take integer values from $-l$ to $+l$, m_j may only take semi-integer values on the interval $[-l - \frac{1}{2}, l + \frac{1}{2}]$. Hence, by the definition of j as $(m_j)_{\max}$, its maximum value has to be $l + \frac{1}{2}$, and for $m_j = l + \frac{1}{2}$, this is the only possible value. This means that the uncoupled state with $m_l = l$ and $m_s = \frac{1}{2}$ should be identical to the coupled-representation state with $j = l + \frac{1}{2}$ and $m_j = l + \frac{1}{2}$:

$$\left| j = l + \frac{1}{2}, m_j = l + \frac{1}{2} \right\rangle = \left| m_l = m_j - \frac{1}{2}, m_s = +\frac{1}{2} \right\rangle. \quad (5.214)$$

⁵² One may think that Eq. (207) is a trivial corollary of Eq. (199). However, now we should be a bit more careful, because in the Clebsch-Gordan coefficients, these quantum numbers characterize different groups of eigenstates.

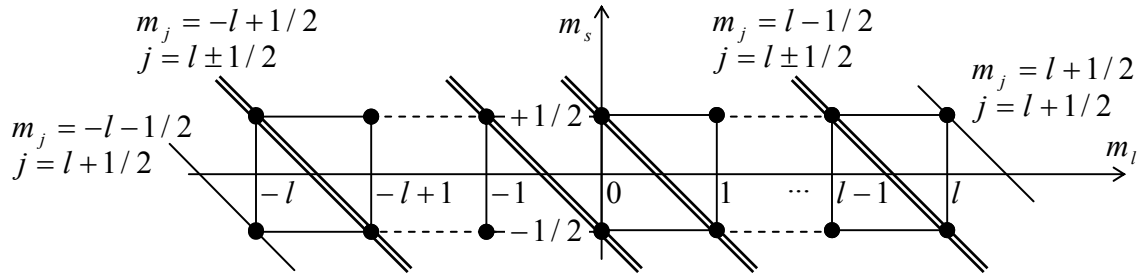


Fig. 5.12. All possible sets of eigenvalues m_l, m_s for a particle with fixed l , and $s = 1/2$. Each uncoupled-representation state is represented by a dot, while each the coupled-representation state, by a single sloped line connecting the dots.

However, already for the next value, $m_j = l - 1/2$, we need to have two values of j , so that two $|m_l, m_s\rangle$ kets is to be related to two $|j, m_j\rangle$ kets by two Clebsch-Gordan coefficients. Since l changes in unit steps, these values of j have to be $l \pm 1/2$. This choice,

$$j = l \pm 1/2, \quad (5.215)$$

evidently satisfies all lower values of m_j (again, with only one value, $j = l + 1/2$, necessary for the lowest $m_j = -l - 1/2$) – see Fig. 12. Note that the total number of the coupled-representation states is $1 + 2 \times 2l + 1 = 2(2l + 1)$, i.e. the same as in the uncoupled representation. So, each sum (210), for fixed j, m_j (and fixed common parameter l), has at most 2 terms, i.e. involves at most 2 Clebsch-Gordan coefficients.

These coefficients may be calculated in a few steps, all but the last one rather simple even for arbitrary spin s . First, the matrix elements of ladder operators $\hat{L}_\pm$ in the standard z -basis (i.e. in the basis of kets $|m_l\rangle$) may be calculated from Eq. (184). Next, the similarity of vector operators $\hat{\mathbf{J}}$ and $\hat{\mathbf{S}}$ to operators $\hat{\mathbf{L}}$, expressed by Eqs. (197), (203), and (204), may be used to argue that the matrix elements of operators $\hat{S}_\pm$ and $\hat{J}_\pm$, defined absolutely similarly to $\hat{L}_\pm$, have similar matrix elements in the bases of kets $|m_s\rangle$ and $|m_j\rangle$, respectively. After that, acting by operator $\hat{J}_\pm = \hat{L}_\pm + \hat{S}_\pm$ upon both parts of Eq. (210), and then inner-multiplying the result by the bra vector $\langle m_l, m_s|$ and using the above matrix elements, we get recurrence relations for the Clebsch-Gordan coefficients. Finally, these relations may be recurrently applied to the adjacent states in both representations, starting from any of the two states common for them – for example, from state with ket-vectors (214), corresponding to the top right point in Fig. 12. Let me leave these straightforward but a bit tedious calculations for reader's exercise and just cite the final result of this procedure for $s = 1/2$:⁵³

$$\begin{aligned} \left\langle m_l = m_j - \frac{1}{2}, m_s = +\frac{1}{2} \left| j = l \pm \frac{1}{2}, m_j \right. \right\rangle &= \pm \left(\frac{l \pm m_j + 1/2}{2l + 1} \right)^{1/2}, \\ \left\langle m_l = m_j + \frac{1}{2}, m_s = -\frac{1}{2} \left| j = l \pm \frac{1}{2}, m_j \right. \right\rangle &= + \left(\frac{l \mp m_j + 1/2}{2l + 1} \right)^{1/2}. \end{aligned} \quad (5.216a)$$

Clebsch -
Gordan
coefficients
for $s = 1/2$

⁵³ For arbitrary spin s , the calculations and even the final expressions for the Clebsch-Gordan coefficients are rather bulky. They may be found, typically in a table form, mostly in special monographs – see, e.g., A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton U. Press, 1957.

For applications, it may be more convenient to use this result in the following equivalent form:

$$\begin{aligned} & \left| j = l \pm \frac{1}{2}, m_j \right\rangle \\ &= \pm \left(\frac{l \pm m_j + 1/2}{2l+1} \right)^{1/2} \left| m_l = m_j - \frac{1}{2}, m_s = +\frac{1}{2} \right\rangle + \left(\frac{l \mp m_j + 1/2}{2l+1} \right)^{1/2} \left| m_l = m_j + \frac{1}{2}, m_s = -\frac{1}{2} \right\rangle. \end{aligned} \quad (5.216b)$$

We will use this relation in Sec. 6.4 for an analysis of the anomalous Zeeman effect, based on the perturbation theory. Moreover, most of the angular momentum addition theory described above is immediately applicable to the addition of angular momenta in multiparticle systems, so we will revisit it in Chapter 8.

To conclude this section, I have to note that the Clebsch-Gordan coefficients (for arbitrary s) participate also in the so-called *Wigner-Eckart theorem* that expresses matrix elements of certain *spherical tensors*, in the coupled-representation basis $|j, m_j\rangle$, via a reduced set of matrix elements. Unfortunately, a discussion of this theorem and its applications would require a higher mathematical background than I can expect from my readers, and more time/space than I can afford.⁵⁴

5.8. Exercise problems

5.1. Use the discussion of Sec. 1 to find an alternative solution of Problem 4.17.

5.2. A two-level system is in a quantum state α , described by ket-vector $|\alpha\rangle = \alpha_\uparrow|\uparrow\rangle + \alpha_\downarrow|\downarrow\rangle$, with given (generally, complex) c -number coefficients $\alpha_\uparrow, \alpha_\downarrow$. Prove that we can always select a 3-component vector $\mathbf{a} = \{a_x, a_y, a_z\}$ of real c -numbers, such that α is an eigenstate of operator $\mathbf{a} \cdot \hat{\boldsymbol{\sigma}}$, where $\hat{\boldsymbol{\sigma}}$ is the operator described, in z -basis, by the Pauli matrix vector. Find all possible values of $\mathbf{a}$ satisfying this condition, and the second eigenstate of operator $\mathbf{a} \cdot \hat{\boldsymbol{\sigma}}$, orthogonal to the given α . Give a Bloch-sphere interpretation of your result.

5.3. A spin- $1/2$ particle is in a constant vertical field, so that its Hamiltonian

$$\hat{H} = \frac{\hbar\Omega}{2} \hat{\sigma}_z,$$

but its spin's initial state is an eigenstate of a different Hamiltonian:⁵⁵

$$\hat{H}_{ini} = \mathbf{a} \cdot \hat{\boldsymbol{\sigma}} \equiv a_x \hat{\sigma}_x + a_y \hat{\sigma}_y + a_z \hat{\sigma}_z.$$

Use any approach you like to calculate the time evolution of the expectation values of the spin components. Interpret the results.

5.4. For any periodic motion of a single particle in a confining potential $U(\mathbf{r})$, the *virial theorem* of nonrelativistic classical mechanics⁵⁶ is reduced to the following equality:

⁵⁴ For the interested reader I can recommend, either Sec. 17.7 in E. Merzbacher, *Quantum Mechanics*, 3rd ed., Wiley, 1998, or Sec. 3.10 in J. Sakurai, *Modern Quantum Mechanics*, Addison-Wesley, 1994.

⁵⁵ Cf. Problems 4.22, 4.23, 5.2.

⁵⁶ See, e.g., CM Problem 1.12.

$$\bar{T} = \frac{1}{2} \overline{\mathbf{r} \cdot \nabla U},$$

where T is particle's kinetic energy, and the top bar means averaging over the period of motion. Prove the quantum-mechanical version of the theorem for an arbitrary stationary quantum state, in the absence of spin effects:

$$\langle T \rangle = \frac{1}{2} \langle \mathbf{r} \cdot \nabla U \rangle,$$

where the angular brackets mean, as everywhere in these notes, the expectation value of the variable inside them.

Hint: Mimicking the proof of the classical virial theorem, consider the time evolution of operator

$$\hat{G} \equiv \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}.$$

5.5. A constant force F is applied to an (otherwise free) 1D particle of mass m . Calculate the eigenfunctions of the problem, using

- (i) the coordinate representation, and
- (ii) the momentum representation.

Discuss the relation between the results.

5.6. The momentum representation of an operator, defined in the Hilbert space of 1D orbital states of a particle, equals p^{-1} . Find its coordinate representation.

5.7.* For a particle moving in a 3D periodic potential, develop the bra-ket formalism for the $\mathbf{q}$ -representation, in which a complex amplitude similar to a_q in Eq. (2.234) (but generalized to 3D and all energy bands) plays the role of the wavefunction. In particular, calculate operators $\mathbf{r}$ and $\mathbf{v}$ in this representation, and use the result to prove Eq. (2.237) for 1D motion in the low-field limit.

Hint: Try to generalize the analysis of the momentum representation in Sec. 5.2.

5.8. In the Heisenberg picture of quantum dynamics, find the operator of velocity and acceleration,

$$\hat{\mathbf{v}} \equiv \frac{d\hat{\mathbf{r}}}{dt} \quad \text{and} \quad \hat{\mathbf{a}} \equiv \frac{d\hat{\mathbf{v}}}{dt},$$

of an electron moving in an arbitrary electromagnetic field. Compare the results with the corresponding classical expressions.

5.9. Calculate, in the WKB approximation, the transmission coefficient T for tunneling of a 2D particle with energy $E < U_0$ through a saddle-shaped potential “pass”

$$U(x, y) = U_0 \left(1 + \frac{xy}{a^2} \right),$$

where U_0 and a are real constants.

5.10. Calculate the so-called *Gamow factor*⁵⁷ for the alpha decay of atomic nuclei, i.e. the exponential factor in the transparency of the tunnel barrier, resulting from the following simple model of the particle's potential energy as a function of its distance from the nuclear center:

$$U(r) = \begin{cases} U_0 < 0, & \text{for } r < R, \\ \frac{ZZ'e^2}{4\pi\epsilon_0 r}, & \text{for } R < r, \end{cases}$$

(where $Ze = 2e > 0$ is the charge of the alpha-particle, $Z'e > 0$ is that of the nucleus after the decay, and R is the nucleus' radius), in the WKB approximation.

5.11. For a 1D harmonic oscillator with mass m and frequency ω_0 , calculate:

- (i) all matrix elements $\langle n | \hat{x}^3 | n' \rangle$, and
- (ii) diagonal matrix elements $\langle n | \hat{x}^4 | n \rangle$,

where n are the Fock states.

5.12. Calculate the sum (over all $n > 0$) of the so-called *oscillator strengths*,

$$f_n \equiv \frac{2m}{\hbar^2} (E_n - E_0) \left| \langle n | \hat{x} | 0 \rangle \right|^2,$$

of quantum transitions between the n^{th} energy level and the ground state, for

- (i) a 1D harmonic oscillator, and
- (ii) a 1D particle confined in an arbitrary stationary potential.

5.13.* Prove the so-called the *Bethe sum rule*,

$$\sum_{n'} (E_{n'} - E_n) \left| \langle n | e^{ikx} | n' \rangle \right|^2 = \frac{\hbar^2 k^2}{2m}$$

(where k is a c -number), valid for a 1D particle moving in an arbitrary time-independent potential $U(x)$, and discuss its relation with the Thomas-Reiche-Kuhn sum rule, whose derivation was the subject of the previous problem.

Hint: Calculate the expectation value, in a stationary state n , of the following double commutator,

$$\hat{D} \equiv \left[\left[\hat{H}, e^{ikx} \right], e^{-ikx} \right],$$

in two ways – first, just spelling out both commutators, and, second, using the commutation relations between operators $\hat{p}$ and $e^{\pm ikx}$, and compare the results.

5.14. Simplify the following operators:

- (i) $\exp\{+ia\hat{x}\} \hat{p}_x \exp\{-ia\hat{x}\}$, and

⁵⁷ Named after G. Gamow, who made this calculation as early as in 1928.

- (ii) $\exp\{+ia\hat{p}_x\}\hat{x}\exp\{-ia\hat{p}_x\}$,
where a is a c -number.

5.15. Use the Heisenberg equation of motion for a direct derivation of time evolution law (5.171) of the creation and annihilation operators of a harmonic oscillator.

5.16. Calculate:

- (i) the expectation value of energy, and
(ii) the laws of time evolution of expectation values of the coordinate and momentum
for a 1D harmonic oscillator, provided that in the initial moment ($t = 0$) it was in state

$$|\alpha\rangle = \frac{1}{\sqrt{2}}(|15\rangle + |16\rangle),$$

where $|n\rangle$ are ket-vectors of the stationary (Fock) states of the oscillator.

5.17.* Re-derive the London dispersion force potential between two 3D harmonic oscillators (already calculated in Problem 3.19), using the language of mutually-induced polarization.

5.18. The discussion of the Glauber state properties in Sec. 5 has used the following general statement: if

$$[\hat{A}, \hat{B}] = \mu\hat{I},$$

where $\hat{A}$ and $\hat{B}$ are arbitrary operators, and μ is an arbitrary c -number, then

$$\exp\{+\hat{A}\}\hat{B}\exp\{-\hat{A}\} = \hat{B} + \mu\hat{I}.$$

Prove the statement.

Hint: One (of several) ways to prove the statement is to expand operator $\hat{f}(\lambda) = \exp\{\lambda\hat{A}\}\hat{B}\exp\{-\lambda\hat{A}\}$ into the Taylor series in c -number λ , and then evaluate it at $\lambda = 1$.

5.19. An external force pulse $F(t)$, of a finite time duration $\mathcal{T}$, is exerted on a 1D harmonic oscillator, initially in its ground state. Use the Heisenberg-picture equations of motion to calculate the expectation value of oscillator's energy at the end of the pulse.

5.20. Calculate the energy of the squeezed ground state ν of a harmonic oscillator, defined by Eq. (172).

5.21. Use Eqs. (5.178) of the lecture notes to prove that operators $\hat{L}_j$ and $\hat{L}^2$ commute with the Hamiltonian of a spinless particle placed in any central potential field.

5.22. Prove the following relations for the operators of the angular momentum:

$$\hat{L}^2 = \hat{L}_z^2 + \hat{L}_+ \hat{L}_- - \hbar \hat{L}_z = \hat{L}_z^2 + \hat{L}_- \hat{L}_+ + \hbar \hat{L}_z.$$

(One of them, Eq. (184), was already used in Sec. 6.)

5.23. According to Eqs. (188) and their discussion, action of the ladder operators on the common eigenkets $|l, m\rangle$ of operators $\hat{L}^2$ and $\hat{L}_z$ may be described as

$$\hat{L}_{\pm}|l, m\rangle = L_{\pm}^{(m)}|l, m \pm 1\rangle.$$

Calculate coefficients $L_{\pm}^{(m)}$, assuming that the eigenstates are normalized: $\langle l, m|l, m\rangle = 1$.

5.24. In the basis of common eigenstates of operators $\hat{L}_z$ and $\hat{L}^2$, described by eigenkets $|l, m\rangle$:

(i) calculate matrix elements $\langle l, m_1|\hat{L}_x|l, m_2\rangle$ and $\langle l, m_1|\hat{L}_x^2|l, m_2\rangle$;

(ii) spell out your results for diagonal matrix elements (with $m_1 = m_2$) and their y -axis counterparts; and

(iii) calculate diagonal matrix elements $\langle l, m|\hat{L}_x\hat{L}_y|l, m\rangle$ and $\langle l, m|\hat{L}_y\hat{L}_x|l, m\rangle$.

5.25. For the state described by the common eigenket $|l, m\rangle$ of operators $\hat{L}_z$ and $\hat{L}^2$ in a reference frame $\{x, y, z\}$, calculate the expectation values $\langle L_z\rangle$ and $\langle L_z^2\rangle$ in the reference frame whose axis z' forms angle θ with axis z .

5.26. Write down the matrices of the following angular momentum operators: $\hat{L}_x, \hat{L}_y, \hat{L}_z$, and $\hat{L}_{\pm}$, in the z -basis of states with $l = 1$.

5.27. Find the angular part of the orbital wavefunction of a particle with a definite value of L^2 , equal to $3\hbar^2$, and the largest possible value of L_x . What is this value?

5.28.* A charged 2D particle is trapped in a soft in-plane potential well $U(x, y) = m\omega_0^2(x^2 + y^2)/2$. Calculate its energy spectrum in the presence of an additional uniform magnetic field $\mathcal{B}$, normal to the plane.

5.29. Calculate the spectrum of rotational energies of an axially-symmetric, rigid molecule.

5.30. For the state with wavefunction $\psi = Cxye^{-\lambda r}$, with a real, positive λ , calculate:

- (i) the expectation values of observables L_x, L_y, L_z and L^2 , and
- (ii) the normalization constant C .

5.31. An angular state of a spinless particle is described by the following ket-vector:

$$|\alpha\rangle = \frac{1}{\sqrt{2}}(|l=3, m=0\rangle + |l=3, m=1\rangle).$$

Find the expectation values of the x - and y -components of its angular momentum. Is it sensitive to a possible phase shift between two component eigenkets?

5.32.* Simplify the following double commutator: $\hat{A}_{jj'} \equiv [\hat{r}_j, [\hat{L}^2, \hat{r}_{j'}]]$.

5.33. Express the commutators listed in Eq. (206), $[\hat{J}^2, \hat{L}_z]$ and $[\hat{J}^2, \hat{S}_z]$, via $\hat{L}_j$ and $\hat{S}_j$.

5.34. Find the operator $\hat{\tau}_\phi$ describing the state rotation by angle ϕ about a certain axis, using the similarity of this operation with the shift of a Cartesian coordinate, discussed in Sec. 5. Then use it to calculate the probabilities of measurements of a beam of particles with z-polarized spin-1/2, by a Stern-Gerlach instrument turned by angle θ within the $[z, x]$ plane (where y is the axis of particle propagation – see Fig. 4.1).⁵⁸

5.35. The rotation (“angle translation”) operators $\hat{\tau}_\phi$, analyzed in the previous problem, and the coordinate translation operator $\hat{\tau}_\lambda$, discussed in Sec. 5.5 of the lecture notes, have a similar structure:

$$\hat{\tau}_\lambda = \exp\left\{-i \frac{\hat{C}\lambda}{\hbar}\right\},$$

where λ is a real c -number, characterizing shift’s magnitude, and $\hat{C}$ is a Hermitian operator that does not explicitly depend on time.

(i) Prove that all such operators $\hat{\tau}_\lambda$ are unitary.

(ii) Prove that if the shift by λ , induced by operator $\hat{\tau}_\lambda$, leaves the Hamiltonian of some system unchanged for any λ , then the variable C , corresponding to the operator $\hat{C}$, is a constant of motion.

(iii) Discuss what does the last conclusion give for the particular operators $\hat{\tau}_x$ and $\hat{\tau}_\phi$.

5.36. A particle is in a state α with the orbital wavefunction proportional to the spherical harmonic $Y_1^1(\theta, \phi)$. Find the angular dependence of the wavefunctions corresponding to the following ket-vectors:

$$(i) \hat{L}_x|\alpha\rangle, \quad (ii) \hat{L}_y|\alpha\rangle, \quad (iii) \hat{L}_z|\alpha\rangle, \quad (iv) \hat{L}_+\hat{L}_-|\alpha\rangle, \quad \text{and} \quad (v) \hat{L}^2|\alpha\rangle.$$

5.37. For a state with definite quantum numbers l and j , prove that observable $\mathbf{L} \cdot \mathbf{S}$ also has a definite value, and calculate this value.

5.38.* Derive the general recurrence relations for the Clebsh-Gordan coefficients.

Hint: Using the similarity of commutation relations, discussed in Sec. 7, generalize the solution of Problem 19 to all angular momentum operators, and apply them to Eq. (198).

5.39. The byproduct of the solution of the previous problem is the general relation for the spin operators (valid for any spin s), which may be rewritten as

⁵⁸ Note that the last task is just a particular case of Problem 4.17 (see also Problem 1).

$$\langle m_s | \hat{S}_\pm | m_s \pm 1 \rangle = \hbar [(s \pm m_s + 1)(s \mp m_s)]^{1/2},$$

provided that all other quantum numbers are fixed. Use this result to spell out the matrices S_x , S_y , S_z , and S^2 of a particle with $s = 1$, in the z -basis - defined as the basis in which the matrix S_z is diagonal.

5.40.* For a particle with spin s , moving in a spherically-symmetric field, find the ranges of possible values of quantum numbers m_j and j , necessary to describe, in the coupled representation basis:

- (i) all states with a definite quantum number l , and
- (ii) a state with definite value of not only l , but also m_l and m_s .

Give an interpretation of your results in terms of the classical geometric vector diagram (see Fig. 11).

5.41. A spin- $1/2$ particle moves in a centrally-symmetric potential $U(r)$. Using Eqs. (216) for the Clebsch-Gordan coefficients,

(i) write explicit expressions for the ket vectors for states that would be simultaneously the eigenstates of operators $\hat{L}^2$, $\hat{J}^2$, and $\hat{J}_z$, via spin eigenkets $|\uparrow\rangle$ and $|\downarrow\rangle$;

(ii) for each such state, find all the possible values of observables L^2 , L_z , S^2 , and S_z , the probability of each listed value, and the expectation value for each of the observables.

5.42. Taking into account electron's spin, find the energy spectrum of an electron, free to move within a plane, besides being placed into a uniform magnetic field $\mathbf{B}$, normal to the plane. Compare the result with the Landau level picture discussed in Sec. 3.2.

Chapter 6. Perturbation Theories

This chapter discusses several perturbative approaches to problems of quantum mechanics, and their simplest applications including the Stark effect, the fine structure of atomic levels, and the Zeeman effect. Moreover, the discussion of the perturbation theory of transitions to continuous spectrum and the Golden Rule of quantum mechanics in the end of this chapter will naturally bring us to the issue of open quantum systems – to be discussed in more detail in the next chapter.

6.1. Eigenvalue/eigenstate problems

Unfortunately, only a few problems of quantum mechanics may be solved exactly in the analytical form. Actually, in the previous chapters we have solved a substantial fraction of such problems for a single particle, and for multi-particle problems the exactly solvable cases are even more rare. However, most practical problems of physics feature a certain small parameter, and this smallness may be exploited by various approximate analytical methods. Earlier in the course, we have explored one of them, the WKB approximation, which is adequate for a particle moving through a slowly changing potential profile. Now I will discuss alternative approaches that are more suitable for other cases. The historic name for these approaches is *the perturbation theory*, but it is more fair to speak about several such theories, because they differ depending on the type of the problem.

The simplest perturbation theories address eigenproblems for systems described by time-independent Hamiltonians of the type

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}, \quad (6.1a)$$

where the *perturbation operator* $\hat{H}^{(1)}$ is “small” - in the sense its addition to the unperturbed operator $\hat{H}^{(0)}$ results in a relatively small change of eigenvalues E_n of the system. A typical problem of this type is the 1D *weakly anharmonic oscillator* (Fig. 1) described by Hamiltonian (1a) with

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \frac{m\omega_0^2}{2} \hat{x}^2, \quad \hat{H}^{(1)} = \alpha \hat{x}^3 + \beta \hat{x}^4 + \dots \quad (6.1b)$$

Weakly
anharmonic
oscillator

with small coefficients $\alpha, \beta, \dots$

I will use the anharmonic oscillator as our first particular example, but let me start from describing the perturbative approach to the general time-independent Hamiltonian (1a). In the bra-ket formalism, the eigenproblem for the perturbed system is

$$(\hat{H}^{(0)} + \hat{H}^{(1)})|n\rangle = E_n|n\rangle. \quad (6.2)$$

Let the eigenstates and eigenvalues of the unperturbed Hamiltonian, which satisfy equation

$$\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle, \quad (6.3)$$

be known. In this case, to solve problem (2) means to find, first, its perturbed eigenvalues E_n and, second, coefficients $\langle n^{(0)}|n\rangle$ of the expansion of perturbed state vectors $|n\rangle$ in series over the unperturbed ones, $|n^{(0)}\rangle$:

$$|n\rangle = \sum_{n'} |n'^{(0)}\rangle \langle n'^{(0)}|n\rangle. \quad (6.4)$$

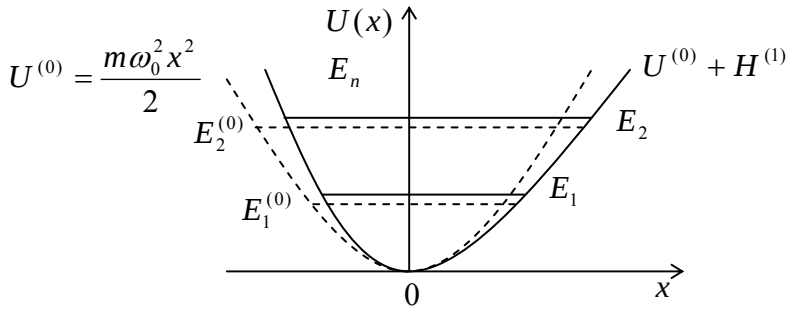


Fig. 6.1. The simplest problem for the perturbation theory application: a 1D weakly anharmonic oscillator. (Dashed lines characterize the unperturbed, harmonic oscillator.)

Let us plug Eq. (4), with the summation index n' replaced with n'' , into both parts of Eq. (2):

$$\sum_{n''} \langle n''^{(0)}|n\rangle \hat{H}^{(0)}|n''^{(0)}\rangle + \sum_{n''} \langle n''^{(0)}|n\rangle \hat{H}^{(1)}|n''^{(0)}\rangle = \sum_{n''} \langle n''^{(0)}|n\rangle E_n |n''^{(0)}\rangle, \quad (6.5)$$

and then inner-multiply all terms by an arbitrary unperturbed ket-vector $\langle n'^{(0)}|$. Assuming that the system of unperturbed eigenstates is orthonormal, $\langle n'^{(0)}|n''^{(0)}\rangle = \delta_{n'n''}$, and using Eq. (3) in the first term of the left-hand part, we get the following system of linear equations

$$\sum_{n''} \langle n''^{(0)}|n\rangle H_{n'n''}^{(1)} = \langle n'^{(0)}|n\rangle (E_n - E_{n'}^{(0)}), \quad (6.6)$$

where the matrix elements of the perturbation are calculated in *unperturbed* bra-kets:

$$H_{n'n''}^{(1)} \equiv \langle n'^{(0)}|\hat{H}^{(1)}|n''^{(0)}\rangle. \quad (6.7)$$

Perturbation's
matrix
elements

The linear equation system (6) is still exact,¹ and is frequently used for numerical calculations. (Since the matrix coefficients (7) typically decrease when n' and/or n'' become very large, the sum in the left-hand part of Eq. (6) may be typically truncated, still giving acceptable accuracy of the solution.) For getting analytical results we need to make more explicit approximations. In the simple perturbation theory we are discussing now, this is achieved by the expansion of both eigenenergies and coefficients into the Taylor series in a certain small parameter μ of the problem:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \dots, \quad (6.8)$$

$$\langle n'^{(0)}|n\rangle = \langle n'^{(0)}|n\rangle^{(0)} + \langle n'^{(0)}|n\rangle^{(1)} + \langle n'^{(0)}|n\rangle^{(2)} \dots, \quad (6.9)$$

where²

$$E_n^{(k)} \propto \langle n'^{(0)}|n\rangle^{(k)} \propto \mu^k. \quad (6.10)$$

¹ Please note its similarity with Eq. (2.215) of the 1D band theory. Indeed, the latter equation is not much more than a particular form of Eq. (6) for 1D wave mechanics, and a specific (periodic) potential $U(x)$ considered as perturbation. Moreover, the approximate treatment of the weak potential limit in Sec. 2.7 was essentially a particular case of the more general perturbation theory we are discussing now.

² Note that, by definition, $\langle n'^{(0)}|n\rangle^{(0)} = \delta_{n'n}$.

In order to explore the 1st-order approximation, which ignores all terms $O(\mu^2)$ and higher, let us plug only the two first terms of expansions (8) and (9) into the basic system of equations (6):

$$\sum_{n''} H_{n'n''}^{(1)} \left(\delta_{n''n} + \langle n''^{(0)} | n \rangle^{(1)} \right) = \left(\delta_{n'n} + \langle n'^{(0)} | n \rangle^{(1)} \right) (E_n^{(0)} + E_n^{(1)} - E_{n'}^{(0)}). \quad (6.11)$$

Now let us open the parentheses, and disregard all the remaining terms $O(\mu^2)$. The result is

$$H_{n'n}^{(1)} = \delta_{n'n} E_n^{(1)} + \langle n'^{(0)} | n \rangle^{(1)} (E_n^{(0)} - E_{n'}^{(0)}), \quad (6.12)$$

This equation is valid for any set of indices n and n' ; let us start from the case $n = n'$ and immediately get a very simple (and the most important!) result:

$$E_n^{(1)} = H_{nn}^{(1)} \equiv \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle. \quad (6.13)$$

For example, let us see what does this result give for two first perturbation terms in the weakly anharmonic oscillator (1b)

$$E_n^{(1)} = \alpha \langle n^{(0)} | \hat{x}^3 | n^{(0)} \rangle + \beta \langle n^{(0)} | \hat{x}^4 | n^{(0)} \rangle. \quad (6.14)$$

As the reader should know from the solution of Problem 5.6, the first term is zero, while the second one yields³

$$E_n^{(1)} = \frac{3}{4} \beta x_0^4 (2n^2 + 2n + 1). \quad (6.15)$$

Naturally, there should be some contribution from the (typically, larger) term proportional to α , so we need to explore the 2nd approximation of the perturbation theory. However, before doing that, let us complete our discussion of its 1st order. For $n' \neq n$, Eq. (12) may be used to calculate the eigenstates rather than the eigenvalues:

$$\langle n'^{(0)} | n \rangle^{(1)} = \frac{H_{n'n}^{(1)}}{E_n^{(0)} - E_{n'}^{(0)}}, \quad \text{for } n' \neq n. \quad (6.16)$$

This means that the eigenket's expansion (4), in the 1st order, may be represented as

$$|n^{(1)}\rangle = \sum_{n' \neq n} \frac{H_{n'n}^{(1)}}{E_n^{(0)} - E_{n'}^{(0)}} |n'^{(0)}\rangle + C |n^{(0)}\rangle. \quad (6.17)$$

Coefficient C cannot be found from Eq. (12), however, requiring the final state n to be normalized, we see that other terms may provide only corrections $O(\mu^2)$, so in the 1st order we should take $C = 1$. The

³ The result for $n = 0$ may be readily calculated in the wave-mechanics style as well, using Eq. (2.269) for unperturbed ground state wavefunction, and the table integral MA Eq. (6.9d):

$$\langle n^{(0)} | \hat{x}^4 | n^{(0)} \rangle_{n=0} = \int (\psi_0^{(0)})^* x^4 \psi_0^{(0)} dx = \left(\frac{1}{\pi x_0} \right)^{1/2} \int_{-\infty}^{+\infty} x^4 \exp \left\{ -\frac{x^2}{x_0^2} \right\} dx = \frac{3}{4} x_0^4,$$

but for higher values of n , such calculations are much harder, because of more involved Eq. (2.279) for $\psi_n^{(0)}$. Note also that at $n \gg 1$, Eq. (15) gives predictions which coincide with those of the classical theory of weakly nonlinear oscillations – see, e.g., CM Sec. 4.2, in particular, Eq. (4.49).

most important feature of Eq. (17) is its denominator: the closer the (unperturbed) eigenenergies of two states, the larger is their mutual contribution (*hybridization*), created by the perturbation.

This feature also affects the 1st approximation's validity condition that may be quantified using Eq. (16): the magnitudes of all the bra-kets it describes have to be much less than the unperturbed product $\langle n|n \rangle^{(0)} = 1$, so that all elements of the perturbation matrix have to be much less than the difference between the corresponding unperturbed energies. For the anharmonic oscillator's energy correction (15), this requirement is reduced to $E_n^{(1)} \ll \hbar\omega_0$.

Now we are ready for going after the 2nd second order approximation to Eq. (6). Let us focus on the case $n' = n$, because as we already know, only this term will give us a correction to eigenenergies. Moreover, we see that since the left-hand side of Eq. (6) already has the small factor $H_{n'n}^{(1)} \propto \mu$, the bra-ket coefficients in that part may be taken from the 1st order result (16). As a result, we get

$$E_n^{(2)} = \sum_{n''} \langle n''^{(0)} | n \rangle^{(1)} H_{nn''}^{(1)} = \sum_{n'' \neq n} \frac{H_{n''n}^{(1)} H_{nn''}^{(1)}}{E_n^{(0)} - E_{n''}^{(0)}}. \quad (6.18)$$

Since $\hat{H}^{(1)}$ represents an observable (energy), and hence has to be Hermitian, we may rewrite this expression as

$$E_n^{(2)} = \sum_{n' \neq n} \frac{|H_{n'n}^{(1)}|^2}{E_n^{(0)} - E_{n'}^{(0)}} = \sum_{n' \neq n} \frac{|\langle n'^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}}. \quad (6.19)$$

2nd - order
correction
for
energies

This is the much celebrated 2nd order perturbation result that frequently (in sufficiently symmetric problems) is the first nonvanishing correction to the state energy – for example, from the cubic term (proportional to α) in our weakly anharmonic oscillator problem (1). In order to calculate the corresponding correction, we may use another result of Problem 5.6:

$$\begin{aligned} \langle n' | \hat{x}^3 | n \rangle &= \left(\frac{x_0}{\sqrt{2}} \right)^3 \\ &\times \left\{ [n(n-1)(n-2)]^{1/2} \delta_{n',n-3} + 3n^{3/2} \delta_{n',n-1} + 3(n+1)^{3/2} \delta_{n',n+1} + [(n+1)(n+2)(n+3)]^{1/2} \delta_{n',n+3} \right\}. \end{aligned} \quad (6.20)$$

So, according to Eq. (19), we need to calculate

$$\begin{aligned} E_n^{(2)} &= \alpha^2 \left(\frac{x_0}{\sqrt{2}} \right)^6 \\ &\times \sum_{n' \neq n} \frac{\left\{ [n(n-1)(n-2)]^{1/2} \delta_{n',n-3} + 3n^{3/2} \delta_{n',n-1} + 3(n+1)^{3/2} \delta_{n',n+1} + [(n+1)(n+2)(n+3)]^{1/2} \delta_{n',n+3} \right\}^2}{\hbar\omega_0(n-n')}. \end{aligned} \quad (6.21)$$

The summation is actually not as cumbersome as may look, because all mixed products are proportional to different Kronecker deltas and hence vanish, so that we need to sum up only the squares of each term:

$$\begin{aligned} E_n^{(2)} &= \frac{\alpha^2}{\hbar\omega_0} \left(\frac{x_0}{\sqrt{2}} \right)^6 \left[\frac{n(n-1)(n-2)}{3} + \frac{9n^3}{1} + \frac{9(n+1)^3}{-1} + \frac{(n+1)(n+2)(n+3)}{-3} \right] \\ &= -\frac{15}{4} \frac{\alpha^2 x_0^6}{\hbar\omega_0} \left(n^2 + n + \frac{11}{30} \right). \end{aligned} \quad (6.22)$$

Please notice that all energy level corrections are negative, regardless of the sign of α . On the contrary, the 1st order correction $E_n^{(1)}$ (15) depends on the sign of parameter β , so that the net correction, $E_n^{(1)} + E_n^{(2)}$, may be of any sign.

Results (17) and (19) are clearly inapplicable to the degenerate case where, in the absence of perturbation, several states correspond to the same energy level, because of the divergence of their denominators.⁴ This divergence hints that the largest effect of the perturbation in that case is the *degeneracy lifting*, e.g., splitting of the initially degenerate energy level $E^{(0)}$ (Fig. 2), and that for the analysis of this case we can, to the first approximation, ignore the effect of all other energy levels. (A careful analysis shows that this is indeed the case until the level splitting becomes comparable with the distance to other energy levels.)

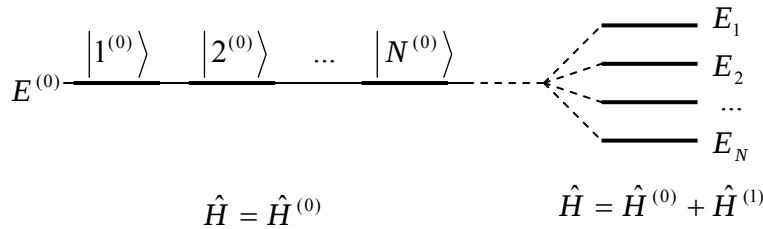


Fig. 5.2. Lifting the energy level degeneracy by a perturbation (schematically).

Limiting the summation in Eq. (6) to the group of N degenerate states with equal $E_n^{(0)} \equiv E(0)$, we reduce it to

$$\sum_{n''=1}^N \langle n''^{(0)} | n \rangle H_{n'n''}^{(1)} = \langle n'^{(0)} | n \rangle (E_n - E^{(0)}). \quad (6.23)$$

where $n'^{(0)}$ and $n''^{(0)}$ number N states of the degenerate group.⁵ Equation (23) may be rewritten as

$$\sum_{n''=1}^N \langle n''^{(0)} | n \rangle (H_{n'n''}^{(1)} - E_n^{(1)} \delta_{n'n''}) = 0, \quad \text{where } E_n^{(1)} \equiv E_n - E^{(0)}. \quad (6.24)$$

For each $n = 1, 2, \dots, N$, this is a system of N linear, homogenous equations (with N terms each) for unknown coefficients $\langle n''^{(0)} | n \rangle$. In this problem, we readily recognize the problem of diagonalization of the perturbation matrix $H^{(1)}$ - cf. Sec. 4.4 and in particular Eq. (4.101). As in the general case, in the condition of self-consistency of the system, we can change the notation of the lower index of $E^{(1)}$, for example to n :

Energy levels of initially degenerate system

$$\begin{vmatrix} H_{11}^{(1)} - E_n^{(1)} & H_{12}^{(1)} & \dots \\ H_{21}^{(1)} & H_{22}^{(1)} - E_n^{(1)} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0.$$

(6.25)

⁴ This is exactly the reason why such perturbation theories run into serious problems for systems with continuous spectrum, and other approximate techniques (such as the WKB approximation) are often necessary.

⁵ Note that the choice of the basis is to some extent arbitrary, because due to the linearity of equations of quantum mechanics, any linear combination of states $n''^{(0)}$ is also an eigenstate of the unperturbed Hamiltonian. However, for using Eq. (24), these combinations have to be orthonormal, as was suggested at the derivation of Eq. (6).

According to the definition (24) of $E_n^{(1)}$, the resulting N energy levels E_n may be found as $E^{(0)} + E_n^{(1)}$, where $E_n^{(1)}$ are the N roots of Eq. (25).

If the perturbation matrix is diagonal, the result is extremely simple,

$$E_n - E^{(0)} \equiv E_n^{(1)} = H_{nn}^{(1)}, \quad (6.26)$$

and formally coincides with Eq. (13) for the non-degenerate case, but now may give a different result for each of N previously degenerate states n .

Let us see what does this theory give for several important examples. First of all, let us consider a two-level system (or a system with two degenerate states with energy far from all others levels), with an *arbitrary* perturbation matrix⁶

$$H^{(1)} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}. \quad (6.27a)$$

Since that both the unperturbed Hamiltonian and the operator of its perturbation are Hermitian, the diagonal elements of matrix $H^{(1)}$ are real, and its off-diagonal elements are complex conjugates of each other. As a result, we can present the matrix in the same form as in Eq. (4.106):

$$H^{(1)} = \begin{pmatrix} a_0 + a_z & a_x - ia_y \\ a_x + ia_y & a_0 - a_z \end{pmatrix} = a_0 I + a_x \sigma_x + a_y \sigma_y + a_z \sigma_z = a_0 I + \mathbf{a} \cdot \boldsymbol{\sigma}. \quad (6.27b)$$

where scalar a_0 and the Cartesian components of vector $\mathbf{a}$ are real c -number coefficients. The corresponding characteristic equation,

$$\begin{vmatrix} a_0 + a_z - E_n^{(1)} & a_x - ia_y \\ a_x + ia_y & a_0 - a_z - E_n^{(1)} \end{vmatrix} = 0, \quad (6.28)$$

has the solution that is familiar to the reader from Chapters 2 and 4:

$$E_{\pm}^{(1)} \equiv E_{\pm} - E^{(0)} = a_0 \pm a = a_0 \pm (a_x^2 + a_y^2 + a_z^2)^{1/2} = \frac{H_{11} + H_{22}}{2} \pm \left[\left(\frac{H_{11} - H_{22}}{2} \right)^2 + H_{12} H_{21} \right]^{1/2}. \quad (6.29)$$

Let us discuss physics of this simple result. Parameter $a_0 = (H_{11} + H_{22})/2$ is evidently the correction to the average energy of both states, that does not give any contribution to the level splitting. The splitting, $\Delta E = E_+ - E_-$, is a hyperbolic function of coefficient $a_z = (H_{11} - H_{22})/2$ that describes the direct contributions (13) to the eigenstates due to the perturbation. A plot of this function is the famous level-anticrossing diagram (Fig. 3) that has already been discussed in Sec. 2.5 in a particular context of the weak potential limit of the 1D band theory – see Fig. 2.29.

Now we see that this is a general result for *any* two-level system. The examples of this behavior that we already know include the coupled quantum wells (see Fig. 2.29 and its discussion), band theory in the weak coupling limit (Sec. 2.5), and spin- $1/2$ systems discussed through Chapter 4 and in Sec. 5.1. By the way, from Sec. 4.4 we already know the perturbed states in the middle of the anticrossing

⁶ For brevity, I am dropping the upper index (1) in the matrix elements.

diagram (at $a_z = 0$). For example, if $a_y = 0$, then our perturbation Hamiltonian matrix (27), besides the trivial term proportional to a_0 , is proportional to σ_x , and hence we can use the result (4.114) to write:⁷

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|1^{(0)}\rangle \pm |2^{(0)}\rangle), \quad (6.30)$$

where $1^{(0)}$ and $2^{(0)}$ are system's states in the absence of the perturbation.

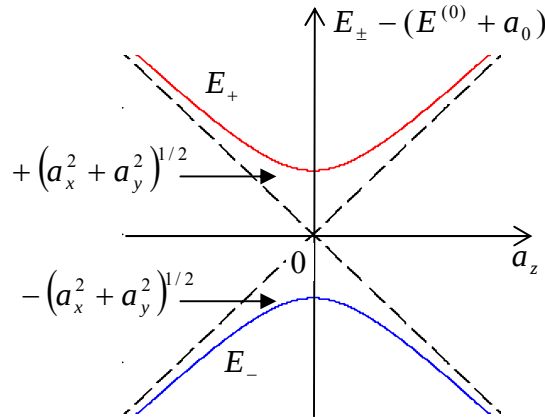


Fig. 6.3. Level-anticrossing diagram for an arbitrary two-level system.

This analysis shows that other results of our discussions of particular two-level systems in Sec. 2.6 and 4.6 are also general. For example, if we put such any two-level system into an initial state different from one of the eigenstates $\pm$, the probability of its finding it in any of states $1^{(0)}$ or $2^{(0)}$ will oscillate with frequency

$$\Omega = \frac{\Delta E}{\hbar} \equiv \frac{E_+ - E_-}{\hbar}. \quad (6.31)$$

Hence, for a spin- $1/2$ particle in a z -oriented magnetic field, the periodic oscillations of the x - and y -components of spin vector, described by Eqs. (4.196) and (4.202), may be interpreted not only as the torque-induced precession of spin within the $[x, y]$ plane, but alternatively as the quantum oscillations of the z -component of spin between states $\uparrow$ and $\downarrow$ with energies $E_{\uparrow}$ and $E_{\downarrow}$ given by Eq. (4.167).

Some other examples of such oscillations may be rather unexpected. For example, the ammonium molecule NH_3 (Fig. 4) has two symmetric states which differ by the inversion of the nitrogen atom relative to the plane of the three hydrogen atoms, and are coupled due to quantum-mechanical tunneling of the nitrogen atom through the plane of hydrogen atoms.⁸ Since for this molecule, the level splitting ΔE corresponds to an experimentally convenient frequency $\Omega/2\pi \approx 24$ GHz, it played an important historic role for the initial development of first atomic frequency standards and microwave quantum generators (*masers*) in the 1950s,⁹ which paved the way toward the development of the laser technology.

⁷ Alternatively, if $a_x = 0$, then $|\pm\rangle = (1/\sqrt{2})(|1^{(0)}\rangle \pm i|2^{(0)}\rangle)$. Note that besides a phase coefficient, these states are similar in that they present a coherent superposition of the unperturbed states, with a 50/50 chance to find the perturbed system in any of those states. In that sense, the effects of perturbation coefficients a_x and a_y are similar.

⁸ Since the hydrogen atoms are much lighter, it is more fair to speak about their correlated tunneling around the (nearly immobile) nitrogen atom.

⁹ In particular, these molecules were used in the demonstration of the first maser by C. Townes' group in 1954.

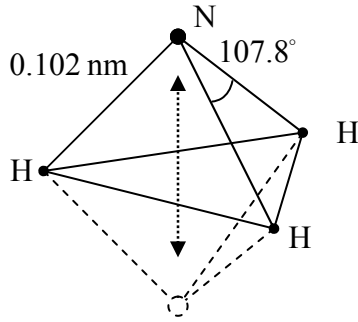


Fig. 6.4. Ammonia molecule and its inversion.

6.2. The Stark effect

Another example of the level degeneracy lifted by a perturbation is the *linear Stark effect* – atomic level splitting by an external electric field. Let us study this effect, in the linear approximation, for a hydrogen-like atom. Taking the direction of external electric field $\mathcal{E}$ (which is practically uniform on the atomic scale) for the z-axis, the perturbation may be represented by the following Hamiltonian:¹⁰

$$\hat{H}^{(1)} = -q\mathcal{E}\hat{z} = -q\mathcal{E}r \cos \theta. \quad (6.32)$$

Stark
effect's
perturbation

(Since we will work in the coordinate representation, we may skip the operator sign from this point on.)

As you (should :-)) remember, energy levels of a hydrogen-like atom depend only on the main quantum number n - see Eq. (3.191); hence all states but the ground state $n = 1$ (“1s” in the spectroscopic nomenclature) in which $l = m = 0$, have some degeneracy that grows rapidly with n . This is why I will carry out the calculations only for the lowest degenerate level with $n = 2$. Since generally $0 \leq l \leq n - 1$, here l may be equal either 0 (one 2s state, with $m = 0$) or 1 (three 2p states, with $m = 0, \pm 1$). Due to this 4-fold degeneracy, $H^{(1)}$ is a 4×4 matrix with 16 elements:

$$H^{(1)} = \begin{matrix} \overbrace{m=0}^{l=0} & \overbrace{m=0 \ m=+1 \ m=-1}^{l=1} \\ \left(\begin{array}{cccc} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{array} \right) & \left. \begin{array}{l} m=0, \quad l=0, \\ m=0, \\ m=+1, \\ m=-1, \end{array} \right\} & l=1. \end{matrix} \quad (6.33)$$

However, please do not be scared. First, due to the Hermitian character of the operator, only 10 of the matrix elements (4 diagonal ones and 6 off-diagonal elements) may be substantially different. Moreover, due to a high symmetry of the problem, there are a lot of zeros even among these elements. Indeed, let us have a look at the angular components Y_l^m of the corresponding wavefunctions, described by Eqs. (3.174)-(3.175). For states with $m = \pm 1$, the azimuthal parts of wavefunctions are proportional to $\exp\{\pm i\phi\}$; hence the off-diagonal elements H_{34} and H_{43} of matrix (33), relating these functions, are proportional to

¹⁰ If there is any doubt why, please revisit the discussion of Eq. (2.247), in which we should now take $F = q\mathcal{E}$.

$$\oint d\Omega Y_1^{\pm*} \hat{H}^{(1)} Y_1^{\mp} \propto \int_0^{2\pi} d\varphi \left(e^{\pm i\varphi} \right)^* \left(e^{\mp i\varphi} \right) = 0. \quad (6.34)$$

The azimuthal-angle symmetry also kills the off-diagonal elements $H_{13}, H_{14}, H_{23}, H_{24}$ (and hence their complex conjugates $H_{31}, H_{41}, H_{32},$ and H_{42}), because they relate states with $m = 0$ and $m \neq 0$, and are proportional to

$$\oint d\Omega Y_1^{0*} \hat{H}^{(1)} Y_1^{\pm 1} \propto \int_0^{2\pi} d\varphi e^{\pm i\varphi} = 0. \quad (6.35)$$

For the diagonal elements H_{33} and H_{44} , corresponding to $m = \pm 1$, the azimuthal-angle integral does not vanish, but since the spherical functions depend on the polar angle as $\sin\theta$, the matrix elements are proportional to

$$\oint d\Omega Y_1^{\pm*} \hat{H}^{(1)} Y_1^{\pm} \propto \int_0^{\pi} \sin\theta d\theta \sin\theta \cos\theta \sin\theta = \int_{-1}^{+1} \cos\theta (1 - \cos^2\theta) d(\cos\theta), \quad (6.36)$$

i.e. are equal to zero as any limit-symmetric integral of an odd function. Finally, for states $2s$ and $2p$ with $m = 0$, the diagonal elements H_{11} and H_{22} are also killed by the polar-angle integration:

$$\oint d\Omega Y_0^{0*} \hat{H}^{(1)} Y_0^0 \propto \int_0^{\pi} \sin\theta d\theta \cos\theta = \int_{-1}^1 \cos\theta d(\cos\theta) = 0, \quad (6.37a)$$

$$\oint d\Omega Y_0^{1*} \hat{H}^{(1)} Y_0^1 \propto \int_0^{\pi} \sin\theta d\theta \cos^3\theta = \int_{-1}^{+1} \cos^3\theta d(\cos\theta) = 0. \quad (6.37b)$$

Hence, the only nonvanishing matrix elements are two off-diagonal elements H_{12} and H_{21} relating different states with $m = 0$, because they are proportional to

$$\oint d\Omega Y_0^{0*} \cos\theta Y_1^0 = \frac{\sqrt{3}}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \cos^2\theta = \frac{1}{\sqrt{3}} \neq 0. \quad (6.38)$$

What remains is to use Eqs. (3.199) for the radial parts of these functions to finish the calculation of those two matrix elements:

$$H_{12} = H_{21} = -\frac{q\mathcal{E}}{\sqrt{3}} \int_0^{\infty} r^2 dr \mathcal{R}_{2,0}(r) r \mathcal{R}_{2,1}(r), \quad (6.39)$$

where the radial functions are given by Eqs. (3.199). Due to the structure of function $\mathcal{R}_{2,0}(r)$, the integral falls into a sum of two parts, both of the type we have already met.¹¹ The final result is

$$H_{12} = H_{21} = 3q\mathcal{E}r_0, \quad (6.40)$$

where r_0 is the radius scale given by Eq. (3.183); for the hydrogen atom it is just the Bohr radius r_B (1.13).

Thus, for our case the perturbation matrix (33) is reduced to

¹¹ See, e.g., MA Eq. (6.7d).

$$H^{(1)} = \begin{pmatrix} 0 & 3q\mathcal{E}r_0 & 0 & 0 \\ 3q\mathcal{E}r_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (6.41)$$

so that the condition (25) of self-consistency is

$$\begin{vmatrix} -E_n^{(1)} & 3q\mathcal{E}r_0 & 0 & 0 \\ 3q\mathcal{E}r_0 & -E_n^{(1)} & 0 & 0 \\ 0 & 0 & -E_n^{(1)} & 0 \\ 0 & 0 & 0 & -E_n^{(1)} \end{vmatrix} = 0, \quad (6.42)$$

giving a very simple characteristic equation

$$(E_n^{(1)})^2 \left[(E_n^{(1)})^2 - (3q\mathcal{E}r_0)^2 \right] = 0. \quad (6.43)$$

with the roots

$$E_{1,2}^{(1)} = 0, \quad E_{3,4}^{(1)} = \pm 3q\mathcal{E}r_0. \quad (6.44)$$

Linear
Stark
effect
for $n = 2$

so that the degeneracy is only partly lifted - see Fig. 5.

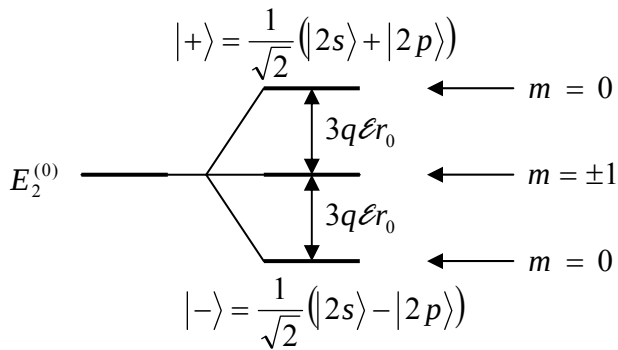


Fig. 6.5. Linear Stark effect for level $n = 2$ of a hydrogen-like atom.

Generally, in order to understand the nature of states corresponding to these levels, we should go back to Eq. (24) with each calculated value of $E_n^{(1)}$, and calculate the corresponding expansion coefficients $\langle n''^{(0)} | n \rangle$, which describe the perturbed states. However, in our simple case the outcome of the procedure is clear in advance. Indeed, since the states with $m = \pm 1$ are not affected by the perturbation (in the linear approximation in electric field), their degeneracy is not lifted, and energy unaffected – see the middle level in Fig. 5. On the other hand, the perturbation matrix connecting states $2s$ and $2p$, i.e. the top left 2×2 part of the full matrix (41), is proportional to the Pauli matrix σ_x , and we already know the result of its diagonalization – see Eqs. (4.114). This means that the upper and lower split levels correspond to very simple linear combinations of the previously degenerate states,

$$|\pm\rangle = \frac{1}{\sqrt{2}} (|2s\rangle \pm |2p\rangle). \quad (6.45)$$

both with $m = 0$.

Finally, let us estimate the magnitude of the linear Stark effect for a hydrogen atom. For a very high electric field of $\mathcal{E} = 3 \times 10^6$ V/m,¹² $q = e \approx 1.6 \times 10^{-19}$ C, and $r_0 = r_B \approx 0.5 \times 10^{-10}$ m, we get a level splitting of $3q\mathcal{E}r_0 \approx 0.8 \times 10^{-22}$ J ≈ 0.5 meV. This number is much lower than the unperturbed energy of the level, $E_2 = -E_H/2 \times 2^2 \approx -3.4$ eV, so that the perturbation result is quite valid. On the other hand, the splitting is much larger than the resolution limit imposed by the natural linewidth ($\sim 10^{-7} E_2$, see Chapter 9), so that the effect is quite observable even in substantially lower electric fields.

6.3. Fine structure of atomic levels

Now let us analyze, for the simplest case of a hydrogen-like atom, the so-called *fine structure* of atomic levels – their degeneracy lifting even in the absence of external fields. In the limit when the effective speed v of electron motion is much smaller than the speed of light c (as it is in the hydrogen atom), the fine structure may be analyzed as a sum of two small relativistic effects. To analyze the first of these effects, let us expand the well-known classical relativistic expression¹³ for the kinetic energy $T = E - mc^2$ of a free particle with the rest mass m ,

$$T = (m^2 c^4 + p^2 c^2)^{1/2} - mc^2 = mc^2 \left[\left(1 + \frac{p^2}{m^2 c^2} \right)^{1/2} - 1 \right], \quad (6.46)$$

into the Taylor series with respect to the small ratio $(p/mc)^2 \approx (v/c)^2$:

$$T = mc^2 \left[1 + \frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 + \dots - 1 \right] = \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots, \quad (6.47)$$

and neglect all the terms besides the first (non-relativistic) one and the next term representing the first nonvanishing relativistic correction of T .

In accordance with the correspondence principle, the quantum-mechanical problem in this approximation may be described by the perturbative Hamiltonian (1a), where the unperturbed (non-relativistic) Hamiltonian of the problem, whose eigenstates and eigenenergies were discussed in Sec. 3.5, is

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \hat{U}(r), \quad \hat{U}(r) = -\frac{C}{r}, \quad (6.48)$$

while the small kinetic-relativistic perturbation is

$$\hat{H}^{(1)} = -\frac{\hat{p}^4}{8m^3 c^2} = -\frac{1}{2mc^2} \left(\frac{\hat{p}^2}{2m} \right)^2. \quad (6.49a)$$

Using Eq. (48), we may rewrite the last formula as

Kinetic-relativistic perturbation

¹² This value approximately corresponds to the threshold of electric breakdown in air, due to the impact ionization on the surface of typical metallic electrodes. (Reducing air pressure only enhances the ionization and lowers the breakdown threshold.) As a result, experiments with higher fields are rather difficult.

¹³ See, e.g., EM Sec. 9.3, in particular Eq. (9.78) - or any undergraduate text on special relativity.

$$\hat{H}^{(1)} = -\frac{1}{2mc^2} \left(\hat{H}^{(0)} - \hat{U}(r) \right)^2, \quad (6.49b)$$

so that its matrix elements, participating in the characteristic equation (25) for a given degenerate energy level (3.191), i.e. a given principal quantum number n , are

$$\langle nlm | \hat{H}^{(1)} | n'l'm' \rangle = -\frac{1}{2mc^2} \langle nlm | \left(\hat{H}^{(0)} - \hat{U}(r) \right) \left(\hat{H}^{(0)} - \hat{U}(r) \right) | n'l'm' \rangle, \quad (6.50)$$

where the bra- and ket vectors describe the unperturbed eigenstates whose eigenfunctions (in the coordinate representation) are given by Eq. (3.190): $\psi_{n,l,m} = \mathcal{R}_{n,l}(r) Y_l^m(\theta, \varphi)$.

It is straightforward (and hence left for the reader :-)) to prove that all off-diagonal elements of the set (50) are equal to 0. Thus we may use Eq. (26) for each set of quantum numbers $\{n, l, m\}$:

$$\begin{aligned} E_{n,l,m}^{(1)} &\equiv E_{n,l,m} - E_n^{(0)} = \langle nlm | \hat{H}^{(1)} | nlm \rangle = -\frac{1}{2mc^2} \left\langle \left(\hat{H}^{(0)} - \hat{U}(r) \right)^2 \right\rangle_{n,l,m} \\ &= -\frac{1}{2mc^2} \left(E_n^2 - 2E_n \langle \hat{U} \rangle_{n,l} + \langle \hat{U}^2 \rangle_{n,l} \right) = -\frac{1}{2mc^2} \left[\frac{E_0^2}{4n^4} - \frac{E_0}{n^2} C \left\langle \frac{1}{r} \right\rangle_{n,l} + C^2 \left\langle \frac{1}{r^2} \right\rangle_{n,l} \right], \end{aligned} \quad (6.51)$$

where index m has been dropped, because the radial wavefunctions $\mathcal{R}_{n,l}(r)$, which affect the averages, do not depend on that quantum number. Now using Eqs. (3.183), (3.191) and the first two of Eqs. (3.201), we finally get

$$E_{n,l}^{(1)} = -\frac{mC^2}{2\hbar^2 c^2 n^4} \left(\frac{n}{l+1/2} - \frac{3}{4} \right) = -\frac{2E_n^2}{mc^2} \left(\frac{n}{l+1/2} - \frac{3}{4} \right). \quad (6.52)$$

Kinetic-relativistic energy correction

Let us discuss this result. First of all, its last form confirms that that correction (52) is indeed much smaller than the unperturbed energy E_n (and hence the perturbation theory is solid) if the latter is much smaller than the relativistic rest energy mc^2 of the particle. Next, since in the Bohr problem $n \geq l+1$, the first fraction in the parentheses of Eq. (52) is always larger than 1, so that the relativistic correction to kinetic energy is negative for all n and l . (This is already evident from Eqs. (6.49), which show that the correction Hamiltonian is a negatively defined form.) Finally, at a fixed principal number n , the negative correction's magnitude decreases with the growth of l . This fact may be classically interpreted using Eq. (3.200): the larger is l (at fixed n), the smaller is particle's average distance from the center, and hence the smaller is its effective velocity, the smaller is the magnitude of the quantum-mechanical average of the negative relativistic correction (49a) to the kinetic energy.

Result (52) is conceptually valid for any physics of interaction $U(r) = -C/r$. However, if the interaction is Coulombic, say between an electron with charge $(-e)$ and a nucleus of charge $(+Ze)$, there is also another relativistic correction to energy, due to the so-called *spin-orbit interaction*. Its physics may be understood from the following semi-qualitative, classical reasoning: from the “the point of view” of an electron rotating about the nucleus at constant distance r with velocity v , it is the nucleus, of charge Ze , that rotates about the electron with velocity $(-v)$ and hence time period $T = 2\pi/v$. From the point of view of magnetostatics, such circular motion of electric charge $Q = Ze$ is equivalent to the

constant circular electric current $I = Qv = (Ze)(v/2\pi r)$ which creates, at electron's location, i.e. in the center of the current loop, a magnetic field with magnitude¹⁴

$$\mathcal{B}_a = \frac{\mu_0}{2r} I = \frac{\mu_0}{2r} \frac{Zev}{2\pi r} = \frac{\mu_0 Zev}{4\pi r^2}. \quad (6.53)$$

The field's direction $\mathbf{n}$ is perpendicular to the apparent plane of the nucleus' rotation (i.e. that of the real rotation of the electron), and hence its vector may be readily expressed via the similarly directed vector $\mathbf{L}$ of electron's angular (orbital) momentum:

$$\mathcal{B}_a = \frac{\mu_0 Zev}{4\pi r^2} \mathbf{n} = \frac{\mu_0 Ze}{4\pi r^3 m_e} m_e v r \mathbf{n} = \frac{\mu_0 Ze}{4\pi r^3 m_e} \mathbf{L} = \frac{Ze}{4\pi \epsilon_0 r^3 m_e c^2} \mathbf{L}, \quad (6.54)$$

where the last transition is due to the basic relation between the SI unit constants: $\epsilon_0 \mu_0 \equiv c^2$.

A more careful (but still classical) analysis of the problem¹⁵ brings both good and bad news. The bad news is that result (54) is wrong by a factor of 2 even for the circular motion, because the electron moves with acceleration, and the reference frame bound to it cannot be considered inertial (as was implied in the above reasoning), so that the actual magnetic field felt by the electron is

$$\mathcal{B} = \frac{Ze}{8\pi \epsilon_0 r^3 m_e c^2} \mathbf{L}. \quad (6.55)$$

The good news is that, so corrected, the result is valid (on the average) for not only circular but arbitrary (elliptic¹⁶) orbital motion in the Coulomb field $U(r)$. Hence from the discussion in Sec. 4.1 and Sec. 4.4 we may expect that the quantum-mechanical description of the interaction between this apparent magnetic field and electron's spin moment (4.116) is given by the following perturbation Hamiltonian

$$\hat{H}^{(1)} = -\hat{\boldsymbol{\mu}} \cdot \hat{\mathcal{B}} = -\left(-\frac{e}{m_e} \hat{\mathbf{S}}\right) \cdot \left(\frac{Ze}{8\pi \epsilon_0 r^3 m_e c^2} \hat{\mathbf{L}}\right) = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi \epsilon_0} \frac{1}{r^3} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}, \quad (6.56a)$$

Spin-orbit
perturbation

where the small correction to value $g_e = 2$ of electron's g -factor has been ignored, because Eq. (56) is already a small correction. This expression is confirmed by the fully-relativistic Dirac theory, to be discussed in Sec. 9.7 below: it yields, for an arbitrary central potential $U(r)$, the following Hamiltonian of the spin-orbit coupling:

$$\hat{H}^{(1)} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dU(r)}{dr} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (6.56b)$$

For the Coulomb potential $U(r) = -Ze^2/4\pi \epsilon_0 r$, this formula is reduced to Eq. (56a).

As we already know from the discussion in Sec. 5.7, such Hamiltonian commutes with all operators diagonal in the coupled representation (inside the blue line in Fig. 5.10): $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$. Hence, using Eq. (5.208) to rewrite the spin-orbit Hamiltonian as

¹⁴ See, e.g., EM Sec. 5.1, in particular, Eq. (5.24).

¹⁵ See, e.g., R. Harr and L. Curtis, *Am. J. Phys.* **55**, 1044 (1987).

¹⁶ See, e.g., CM Sec. 3.6.

$$\hat{H}^{(1)} = \frac{1}{2mm_e^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \frac{1}{2} (\hat{j}^2 - \hat{L}^2 - \hat{S}^2), \quad (6.57)$$

we may conclude that this operator is diagonal in the coupled representation with fixed quantum numbers l, s, j , and m_j . As a result, in this representation, we may again use Eq. (26) for each set $\{l, j, m_j\}$:

$$E_{n,j,l}^{(1)} = \frac{1}{2mm_e^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n,l} \frac{1}{2} \langle \hat{j}^2 - \hat{L}^2 - \hat{S}^2 \rangle_{j,s}, \quad (6.58)$$

where the indices irrelevant for each particular term have been dropped. (As a reminder, the spin quantum number s is fixed by particle's nature; for our case of an electron, $s = 1/2$.) Now using the last of Eqs. (3.201), and similar expressions (5.192), (5.197), and (5.203), we get an explicit expression for the spin-orbit corrections¹⁷

$$E_{n,j,l}^{(1)} = \frac{1}{2m_e^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{\hbar^2}{2r_0^3} \frac{j(j+1) - l(l+1) - 3/4}{n^3l(l+1/2)(l+1)} = \frac{E_n^2}{m_e c^2} n \frac{j(j+1) - l(l+1) - 3/4}{l(l+1/2)(l+1)}. \quad (6.59)$$

Spin-orbit
energy
correction

The last form of its right-hand part shows very clearly that this correction has the same scale as the kinetic correction (52),¹⁸ so that they should be considered together. In the first order of the perturbation they may be just added, giving a very simple formula for the net fine structure of level n :

$$E_{\text{fine}}^{(1)} = \frac{E_n^2}{2m_e c^2} \left(3 - \frac{4n}{j+1/2} \right). \quad (6.60)$$

Fine
structure
of H-like
atom's
levels

This simplicity, as well as the independence of the result of the orbital quantum number l , will become less surprising when (in Sec. 9.7) we see that this formula follows in one shot from the Dirac theory, in which the Bohr atom's energy spectrum is numbered only with n and j , but not l .

Let us recall (see Sec. 5.7) that for an electron ($s = 1/2$), the quantum number j may take n positive half-integer values, from $1/2$ to $n - 1/2$. With the account of this fact, Eq. (60) shows that the fine structure of n^{th} Bohr's energy level has n sub-levels – see Fig. 6.

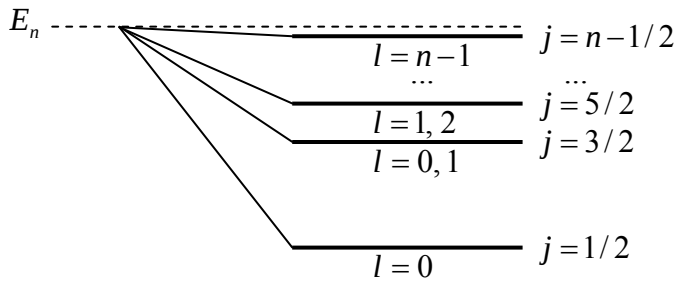


Fig. 6.6. Fine structure of a hydrogen-like atom's level.

¹⁷ The factor l in the denominator does not give a divergence at $l = 0$, because in this case $j = s = 1/2$, and the nominator turns into 0 as well. A careful analysis of this case (which may be found, e.g., in G. K. Woolgate, *Elementary Atomic Structure*, 2nd ed., Oxford, 1983), as well as the exact solution of the Bohr atom problem within the Dirac theory (Chapter 9) show that the final result (60), which is independent of l , is valid even in this case.

¹⁸ This is natural, because the magnetic interaction of charged particles is an essentially relativistic effect, of the same order ($\sim v^2/c^2$) as the kinetic correction (49a) – see, e.g., EM Sec. 5.1, in particular Eq. (5.3).

Please note that according to Eq. (5.203), each of these sub-levels is still $(2j + 1)$ -times degenerate in quantum number m_j . This degeneracy is very natural, because in the absence of external field the system is still isotropic. Moreover, on each fine-structure level, besides the lowest ($j = 1/2$) and the highest ($j = n - 1/2$) ones, each of the m_j -states is doubly-degenerate in the orbital quantum number $l = j \mp 1/2$ - see the labels of l in Fig. 6. (According to Eq. (5.215), each of these states, with fixed j and m_j , may be represented as a linear combination of two states with adjacent values of l , and hence different electron spin orientations, $m_s = \pm 1/2$, weighed with the Clebsch-Gordan coefficients.)

These details aside, one may crudely say that the relativistic corrections make the total eigenenergy to grow with l , contributing to the effect already mentioned at our analysis of the periodic table of elements in Sec. 3.7. The relative scale of this increase may be evaluated from the largest deviation from the unperturbed energy E_n , reached for the state with $j = 1/2$ (and hence $l = 0$):

$$\frac{|E_{\max}^{(1)}|}{E_n} = \frac{E_n}{m_e c^2} \left(2n - \frac{3}{2} \right) = \left(\frac{Ze^2}{4\pi\epsilon_0 \hbar c} \right)^2 \left(\frac{1}{n} - \frac{3}{4n^2} \right) = Z^2 \alpha^2 \left(\frac{1}{n} - \frac{3}{4n^2} \right). \quad (6.61)$$

where α is the fine structure (“Sommerfeld”) constant,

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}, \quad (6.62)$$

that was already mentioned in Sec. 4.4.¹⁹ These expressions show that the fine structure is indeed a relatively small correction ($\sim \alpha^2$) for the hydrogen atom, but it rapidly grows (as Z^2) with the nuclear charge (atomic number), and becomes rather substantial for the heaviest atoms with $Z \sim 100$.

6.4. The Zeeman effect

Now, we are ready to review the *Zeeman effect* - the lifting of atomic level degeneracy by an external magnetic field.²⁰ Using Eq. (3.26) (with $q = -e$) for the description of electron’s orbital motion in the field, and Eq. (4.116) for the operator of electron’s magnetic moment due to its spin- $1/2$, we see that even for a hydrogen-like (i.e. single-electron) atom, neglecting the relativistic effects, the full Hamiltonian is rather bulky:

$$\hat{H} = \frac{1}{2m_e} (\hat{\mathbf{p}} + e\hat{\mathbf{A}})^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{e}{m_e} \hat{\mathbf{B}} \cdot \hat{\mathbf{S}}. \quad (6.63)$$

There are several simplifications we may make. First, let us assume that the external field is spatial-uniform on the atomic scale (which is a very good approximation for most cases), so that we can take the vector-potential in an axially-symmetric gauge – cf. Eq. (3.132):

¹⁹ See the *Selected Physical Constants* appendix for the more exact value of this constant. Its expression in Gaussian units, $\alpha = e^2/\hbar c$, makes even more evident the fact that α is the just fundamental constant ratio which characterizes the strength (or rather the weakness :-)) of electromagnetic effects in quantum mechanics - that in particular makes the perturbative quantum electrodynamics possible. The alternative expression $\alpha = E_H/m_e c^2$, where E_H is the Hartree energy (1.9), the scale of all E_n , is also very revealing.

²⁰ It was discovered experimentally in 1896 by P. Zeeman who, amazingly, was fired from the University of Leiden for an unauthorized use of lab equipment for this work – just to receive a Nobel Prize for it in a few years.

$$\mathbf{A} = \frac{1}{2} \mathcal{B} \times \mathbf{r}. \quad (6.64)$$

Second, let us neglect the terms proportional to $\mathcal{B}^2$, which are small in practical magnetic fields of the order of a few Tesla.²¹ The remaining term in the effective kinetic energy, describing the interaction with the magnetic field, is linear in the momentum operator, so that we may repeat the standard classical calculation²² to reduce it to the product of $\mathcal{B}$ by the orbital magnetic moment's component $m_z = -eL_z/2m_e$ - besides that both m_z and L_z should be understood as operators now. As a result, the Hamiltonian reduces to Eq. (1a), $\hat{H}^{(0)} + \hat{H}^{(1)}$, where $\hat{H}^{(0)}$ is that of the atom at $\mathcal{B}=0$, and

$$\hat{H}^{(1)} = \frac{e\mathcal{B}}{2m_e} (\hat{L}_z + 2\hat{S}_z). \quad (6.65) \quad \text{Zeeman effect's perturbation}$$

The form of the perturbation immediately reveals the major complication with the Zeeman effect description. Namely, in comparison with its contribution (5.198) to the total angular momentum of the electron, its spin-1/2 produces a twice larger contribution into the magnetic moment, so that the right-hand part of Eq. (65) is *not* proportional to the total angular momentum. As a result, the effect description is simple only in two limits.

If the magnetic field is so *high* that its effects are much stronger than the relativistic (fine-structure) effects discussed in the last section, we may treat two terms in Eq. (48) as independent perturbations of different (orbital and spin) degrees of freedom. Since in the z-basis each of the perturbation matrices is diagonal, we can again use Eq. (26):

$$\begin{aligned} E - E^{(0)} &= \frac{e\mathcal{B}}{2m_e} (\langle n, l, m_l | \hat{L}_z | n, l, m_l \rangle + 2\langle m_s | \hat{S}_z | m_s \rangle) = \frac{e\mathcal{B}}{2m_e} (\hbar m_l + 2\hbar m_s) \\ &= \mu_B \mathcal{B} (m_l \pm 1). \end{aligned} \quad (6.66) \quad \text{Paschen-Back effect}$$

This result describes splitting of each $2 \times (2l + 1)$ -degenerate energy level, with certain n and l , into $(2l + 3)$ levels (Fig. 7), with the adjacent level splitting of $\mu_B \mathcal{B}$, equal to $\sim 10^{-23} \text{ J} \sim 10^{-4} \text{ eV/T}$. Note that all levels, besides the top and bottom one, remain doubly degenerate. This limit of the Zeeman effect is sometimes called the *Paschen-Back effect* – which simplicity was recognized only in the 1920s, due to the need in very high magnetic fields for its observation.

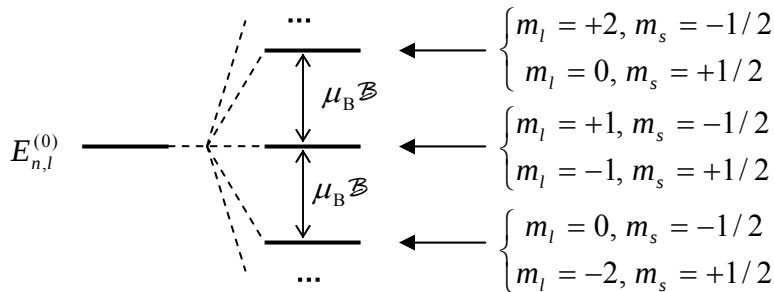


Fig. 6.7. The Paschen-Back effect.

²¹ Despite its smallness, the quadratic term is necessary for description of the negative contribution of the orbital motion to the magnetic susceptibility χ_m (the so-called *orbital diamagnetism*, see EM Sec. 5.5), whose analysis, using Eq. (63), is left for reader's exercise.

²² See, e.g., EM Sec. 5.4, in particular Eqs. (5.95) and (5.100).

In the opposite limit of *low* magnetic field, the Zeeman effect takes place on the background of the fine structure splitting. As was discussed in Sec. 3, at $\mathcal{B} = 0$ each split sub-level has a $2(2l + 1)$ -fold degeneracy corresponding to $(2l + 1)$ different values of the half-integer quantum number m_j , ranging from $-j$ to $+j$, and 2 values of integer $l = j \mp \frac{1}{2}$ - see Fig. 6. The magnetic field lifts this degeneracy.²³ Indeed, in the coupled representation discussed in Sec. 5.7, perturbation (48) is described by the matrix with elements

$$\begin{aligned} H^{(1)} &= \frac{e\mathcal{B}}{2m_e} \langle j, m_j | \hat{L}_z + 2\hat{S}_z | j', m_{j'} \rangle = \frac{e\mathcal{B}}{2m_e} \langle j, m_j | \hat{J}_z + \hat{S}_z | j', m_{j'} \rangle \\ &= \frac{e\mathcal{B}}{2m_e} \left(\hbar m_j \delta_{m_j m_{j'}} + \langle j, m_j | \hat{S}_z | j', m_{j'} \rangle \right). \end{aligned} \quad (6.67)$$

Now plugging into the last term the Clebsh-Gordan expansions (5.216a) for the bra- and ket-vectors, and taking into account that operator $\hat{S}_z$ gives non-zero bra-kets only for $m_s = m'_s$, matrix (67) becomes diagonal, and may again use Eq. (26) to get

Anomalous
Zeeman
effect
for $s = 1/2$

$$\begin{aligned} E - E^{(0)} &= \frac{e\mathcal{B}}{2m_e} \left[\hbar m_j + \frac{\hbar}{2} \frac{(l \pm m_j + 1/2)}{2l + 1} - \frac{\hbar}{2} \frac{(l \mp m_j + 1/2)}{2l + 1} \right] \\ &= \frac{e\mathcal{B}}{2m_e} \hbar m_j \left(1 \pm \frac{1}{2l + 1} \right) = \mu_B \mathcal{B} m_j \left(1 \pm \frac{1}{2l + 1} \right), \quad \text{for } -j \leq m_j \leq +j, \end{aligned} \quad (6.68)$$

where two signs correspond to the two possible values of $l = j \mp \frac{1}{2}$ - see Fig. 8.

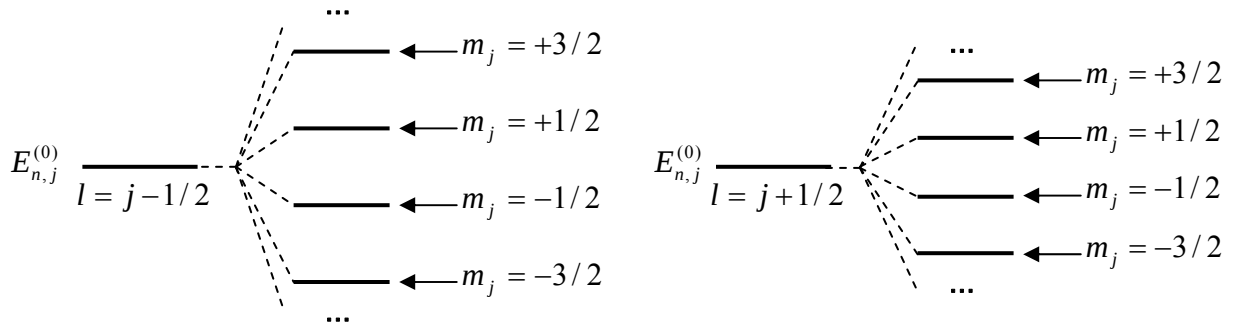


Fig. 6.8. Anomalous Zeeman effect in a hydrogen-like atom – schematically.

We see that the magnetic field splits each sub-level of the fine structure, with a given l , into $2j + 1$ levels, with the distance between the levels depending on l . In the end of the 1890s, when the Zeeman effect was first observed, there was no notion of spin at all, so that this puzzling result was called the *anomalous Zeeman effect*. (In this terminology, the *normal Zeeman effect* is the one with no spin splitting, i.e. without the second terms in the parentheses of Eqs. (66)-(68); it may be observed experimentally in atoms with the net spin $s = 0$.)

²³ In almost-hydrogen-like, but more complex atoms (such as those of alkali metals), the degeneracy in l is lifted by electron-electron interaction even in the absence of the external magnetic field.

The strict quantum-mechanical analysis of the anomalous Zeeman effect for arbitrary s (which is important for applications to multi-electron atoms) is not that complex, but requires explicit expressions for the corresponding Clebsch-Gordan coefficients, which are rather bulky. Let me just cite the unexpectedly simple result of this analysis:

$$\Delta E = \mu_B \mathcal{B} m_j g, \quad (6.69)$$

where g is the so-called *Lande factor*:²⁴

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \quad (6.70)$$

Anomalous
Zeeman
effect
for arbitrary s

For $s = 1/2$ (and hence $j = l \pm 1/2$), this factor is reduced to the parentheses in the last form of Eq. (68).

It is remarkable that Eqs. (69)-(70) may be readily derived using very plausible classical arguments, similar to those used in Sec. 5.7 - see Fig. 5.11 and its discussion. As we have seen above, in the absence of spin, the quantization of observable L_z is an extension of the classical torque-induced precession of the corresponding vector (say, $\mathbf{L}$) about the magnetic field direction, so that the interaction energy, proportional to $\mathcal{A}_{L_z} = \mathcal{B} \cdot \mathbf{L}$, remains constant (Fig. 9a). At the spin-orbit interaction without external magnetic field, the Hamiltonian includes the operator of product $\mathbf{S} \cdot \mathbf{L}$, so that it has to be quantized, i.e. constant, together with J^2 , L^2 , and S^2 . Hence, this system's classical image is a rapid precession of vectors $\mathbf{S}$ and $\mathbf{L}$ about the direction of vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$, so that the spin-orbit interaction energy, proportional to product $\mathbf{L} \cdot \mathbf{S}$, remains constant (Fig. 9b). On this backdrop, the anomalous Zeeman effect in a relatively weak magnetic field $\mathcal{B} = \mathcal{B}_z \mathbf{e}_z$ corresponds to a slow precession of vector $\mathbf{J}$ ("dragging" the rapidly rotating vectors $\mathbf{L}$ and $\mathbf{S}$ with it) about axis z .

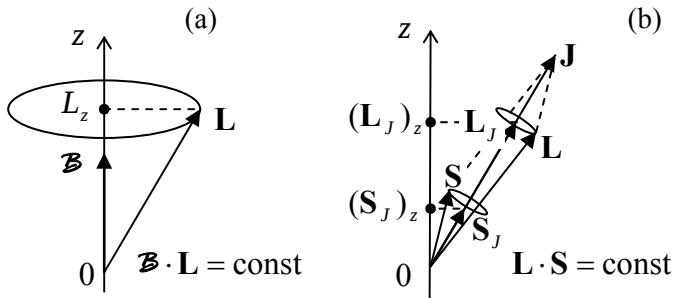


Fig. 6.9. Classical images of (a) the orbital angular momentum's quantization in external magnetic field and (b) the fine-structure level splitting.

This picture allows us to conjecture that what is important for the slow precession rate are only the vectors $\mathbf{L}$ and $\mathbf{S}$ averaged over the period of the much faster precession about vector $\mathbf{J}$ - in other words, only their components $\mathbf{L}_J$ and $\mathbf{S}_J$ directed along vector $\mathbf{J}$. Classically, these components may be calculated as

$$\mathbf{L}_J = \frac{\mathbf{L} \cdot \mathbf{J}}{J^2} \mathbf{J}, \quad \mathbf{S}_J = \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \mathbf{J}. \quad (6.71)$$

The scalar products participating in these expressions may be readily expressed via the squared length of the vectors, using the following evident formulas:

²⁴ This formula is frequently used with capital letters J , S , and L , which denote the quantum numbers of the atom as a whole.

$$S^2 = (\mathbf{J} - \mathbf{L})^2 = J^2 + L^2 - 2\mathbf{L} \cdot \mathbf{J}, \quad L^2 = (\mathbf{J} - \mathbf{S})^2 = J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}. \quad (6.72)$$

As a result, we get the following time average:

$$\begin{aligned} \overline{L_z + 2S_z} &= (\mathbf{L}_J + 2\mathbf{S}_J)_z = \left(\frac{\mathbf{L} \cdot \mathbf{J}}{J^2} \mathbf{J} + 2 \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \mathbf{J} \right)_z = \frac{J_z}{J^2} (\mathbf{L} \cdot \mathbf{J} + 2\mathbf{S} \cdot \mathbf{J}) \\ &= J_z \frac{(J^2 + L^2 - S^2) + 2(J^2 + S^2 - L^2)}{2J^2} = J_z \left(1 + \frac{J^2 + S^2 - L^2}{2J^2} \right). \end{aligned} \quad (6.73)$$

The last move is to smuggle in some quantum mechanics by using, instead of vector lengths squared, and the z-component of J_z , their eigenvalues given by Eqs. (5.197), (5.203), and (5.204). As a result, we immediately arrive at the exact result given by Eqs. (69)-(70). This coincidence encourages thinking about quantum mechanics of angular momenta in classical terms of torque-induced precession, and turns out to be very fruitful in more complex problems of atomic and molecular physics.

The high-field limit and low-field limits of the Zeeman effect, described respectively by Eqs. (66) and (68), are separated by a medium field strength range in which the Zeeman splitting is of the order of the fine-structure splitting analyzed in Sec. 3. There is no time in this course for a quantitative analysis of this crossover.²⁵

6.5. Time-dependent perturbations

Now let us proceed to the case when perturbation $\hat{H}^{(1)}$ in Eq. (1a) is a function of time, while $\hat{H}^{(0)}$ is time-independent. The adequate perturbative approach to this problem, and its results, depend critically on the relation between the characteristic frequency (or the characteristic reciprocal time) ω of the perturbation and the distance between the initial system's energy levels:

$$\hbar\omega \leftrightarrow |E_n - E_{n'}|. \quad (6.74)$$

In the easiest case when all essential frequencies of a perturbation are very small in the sense of Eq. (74), we are dealing with the so-called *adiabatic* change of parameters, that may be treated essentially as a time-independent perturbation (see the previous sections of this chapter). The most interesting observation here is that the adiabatic perturbation does not allow any significant transfer of system's probability from one eigenstate to another. For example, in the WKB limit of the orbital motion, the Bohr-Sommerfeld quantization rule (2.110), and its multi-dimensional generalization, guarantee that integral

$$\oint_C \mathbf{p} \cdot d\mathbf{r}, \quad (6.75)$$

taken along the particle's classical trajectory, is an *adiabatic invariant*, i.e. does not change at a slow change of system's parameters. (It is curious that classical mechanics also guarantees the invariance of integral (75), but its proof there²⁶ is much harder than the quantum-mechanical derivation of this fact,

²⁵ For a more complete discussion of the Stark, Zeeman, and fine-structure effects in atoms, I can recommend, for example, either the monograph by G. Woolgate cited above, or the one by I. Sobelman, *Theory of Atomic Spectra*, Alpha Science, 2006.

²⁶ See, e.g., CM Sec. 10.2.

carried out in Sec. 2.4.) This is why even if the perturbation becomes large with time (while changing sufficiently slowly), we can expect the eigenstate and eigenvalue classification to persist.

Now let us proceed to the more important (and more complex) case when both sides of Eq. (74) are comparable, and use for its discussion the Schrödinger picture of quantum mechanics given by Eqs. (4.157) and (4.158). Combining these equations, we get the Schrödinger equation in the form

$$i\hbar \frac{\partial}{\partial t} |\alpha(t)\rangle = (\hat{H}^{(0)} + H^{(1)}(t)) |\alpha(t)\rangle. \quad (6.76)$$

Very much in the spirit of our treatment of the time-independent case in Sec. 1, let us represent the time-dependent ket-vector of the system with its expansion,

$$|\alpha(t)\rangle = \sum_n |n\rangle \langle n|\alpha(t)\rangle, \quad (6.77)$$

over the full and orthonormal set of the unperturbed, stationary ket-vectors defined by equation

$$\hat{H}^{(0)} |n\rangle = E_n |n\rangle, \quad (6.78)$$

where bra-kets $\langle n|\alpha(t)\rangle$ are time-dependent coefficients. Plugging expansion (77), with n replaced with n' , into both sides of Eq. (76), and then inner-multiplying both its parts by bra-vector $\langle n|$ of another unperturbed (and hence time-independent) state of the system, we get a set of linear, ordinary differential equations for the expansion coefficients:

$$i\hbar \frac{d}{dt} \langle n|\alpha(t)\rangle = E_n \langle n|\alpha(t)\rangle + \sum_{n'} H_{nn'}^{(1)}(t) \langle n'|\alpha(t)\rangle, \quad (6.79)$$

where the matrix elements of the perturbation in the unperturbed state basis, defined similarly to Eq. (7), are now functions of time:

$$H_{nn'}^{(1)}(t) \equiv \langle n|\hat{H}^{(1)}(t)|n'\rangle. \quad (6.80)$$

The set of differential equations (79), which are still exact, may be useful for numerical calculations, because for virtually all practical problems the set of eigenstates n' may be restricted with an acceptable error in the final result.²⁷ However, Eq. (79) has a certain technical inconvenience, which becomes clear if we consider its (evident) solution in the absence of perturbation:²⁸

$$\langle n|\alpha(t)\rangle = \langle n|\alpha(0)\rangle \exp\left\{-i \frac{E_n}{\hbar} t\right\}. \quad (6.81)$$

We see that the solution oscillates very fast, and its numerical modeling may present a challenge for even fastest computers. These spurious oscillations (whose frequency, in particular, depends of the energy reference level) may be partly tamed by looking for the general solution of Eqs. (79) in a form inspired by Eq. (81):

²⁷ Even if the problem under analysis may be described by the wave-mechanics Schrödinger equation (1.25), a direct numerical integration of that *partial* differential equation is typically less convenient than that of the *ordinary* differential equations (79).

²⁸ This is of course just a more general form of Eq. (1.61) of wave mechanics of time-independent systems.

$$\langle n | \alpha(t) \rangle \equiv a_n(t) \exp \left\{ -i \frac{E_n}{\hbar} t \right\}. \quad (6.82)$$

Here $a_n(t)$ are new functions of time (essentially, the stationary states' probability amplitudes), which may be used, in particular, to calculate the time-dependent *level occupancies*, i.e. the probabilities W_n to find the perturbed system on the corresponding energy levels of the unperturbed system:

$$W_n(t) = |\langle n | \alpha(t) \rangle|^2 = |a_n(t)|^2. \quad (6.83)$$

Plugging Eq. (65) into Eq. (79), for these functions we readily get a slightly modified system of equations:

$$i\hbar \dot{a}_n = \sum_{n'} a_{n'} H_{nn'}^{(1)}(t) \exp \left\{ i \frac{E_n - E_{n'}}{\hbar} t \right\} \equiv \sum_{n'} a_{n'} H_{nn'}^{(1)}(t) e^{i\omega_{nn'} t}, \quad (6.84)$$

General
equations
for
probability
amplitude
evolution

where factors $\omega_{nn'}$, defined by relation

$$\hbar \omega_{nn'} \equiv E_n - E_{n'}, \quad (6.85)$$

have the physical sense of frequencies of *potential* quantum transitions between the n -th and n' -th energy levels of the unperturbed system. (The conditions when such transitions indeed take place will be discussed later in this chapter.) An advantage of Eq. (84) over Eq. (79) for numerical calculations is the absence of any dependence on the energy reference selection, and lower frequencies of oscillations of the right hand part terms, especially when the energy levels of interest are close to each other.

In order to continue our analytical treatment, let us restrict ourselves to a particular but very important case of a sinusoidal perturbation *turned on* at some moment - for example, at $t = 0$:

$$\hat{H}^{(1)}(t) = \begin{cases} 0, & \text{for } t < 0, \\ \hat{A} e^{-i\omega t} + \hat{A}^\dagger e^{+i\omega t}, & \text{for } t \geq 0, \end{cases} \quad (6.86)$$

Turning on
sinusoidal
perturbation

where the *perturbation amplitude operators* $\hat{A}$ and $\hat{A}^\dagger$, and hence their matrix elements,

$$\langle n | \hat{A} | n' \rangle \equiv A_{nn'}, \quad \langle n | \hat{A}^\dagger | n' \rangle = A_{n'n}^*, \quad (6.87)$$

are time-independent.²⁹ In this case, for $t > 0$, Eq. (84) yields

$$i\hbar \dot{a}_n = \sum_{n'} a_{n'} \left[A_{nn'} e^{i(\omega_{nn'} - \omega)t} + A_{n'n}^* e^{i(\omega_{nn'} + \omega)t} \right]. \quad (6.88)$$

This is, generally, still a complex system of coupled differential equations; however, it allows simple and explicit solutions in two very important cases. First, let us assume that our system is initially in one eigenstate n' (say, on the ground energy level), and that the occupancies W_n of all other levels stays very low all the time. (We will find the corresponding condition *a posteriori* - from the solution.) With the corresponding assumption

²⁹ The notation of the amplitude operators in Eq. (86) is justified by the fact that the perturbation Hamiltonian has to be self-adjoint (Hermitian), and hence each term in the right-hand part of that relation has to be a Hermitian conjugate of its counterpart, which is evidently true only if the amplitude operators are also the Hermitian conjugates of each other. Note, however, that each of the amplitude operators is generally *not* Hermitian.

$$a_{n'} = 1; \quad |a_n| \ll 1, \quad \text{for } n \neq n', \quad (6.89)$$

Eq. (88) may be readily integrated, giving

$$a_n = -\frac{A_{nn'}}{\hbar(\omega_{nn'} - \omega)} \left[e^{i(\omega_{nn'} - \omega)t} - 1 \right] - \frac{A_{n'n}^*}{\hbar(\omega_{nn'} + \omega)} \left[e^{i(\omega_{nn'} + \omega)t} - 1 \right], \quad \text{for } n \neq n'. \quad (6.90)$$

We see that the probability W_n (83) of finding the system on each energy level of the system oscillates in time, and that our assumption (89) is satisfied as soon as the excitation amplitude is not too large,³⁰

$$|A_{nn'}| \ll \hbar|\omega \pm \omega_{nn'}|. \quad (6.91)$$

Expression (90) also shows that this phenomenon has a clearly resonant character: the maximum occupancy W_n of a level grows infinitely when the corresponding *detuning*,³¹

$$\Delta_{nn'} \equiv \omega - \omega_{nn'}, \quad (6.92)$$

tends to zero. In this limit, our initial assumption (89) may become a liability; in order to overcome it we may perform the following trick - very similar to the one we used for transfer to the degenerate case in Sec. 1. Let us assume that for a certain level n ,

$$|\Delta_{nn'}| \ll \omega, |\omega \pm \omega_{n''n}|, |\omega \pm \omega_{n''n'}|, \quad \text{for all } n'' \neq n, n' \quad (6.93)$$

- the condition illustrated in Fig. 10. Then, according to Eq. (90), we may ignore the occupancy of all but two levels, n and n' , and also the second, non-resonant terms with frequency $\omega_{nn'} + \omega \approx 2\omega \gg |\Delta_{nn'}|$ in Eqs. (88) written for a_n and $a_{n'}$.³²

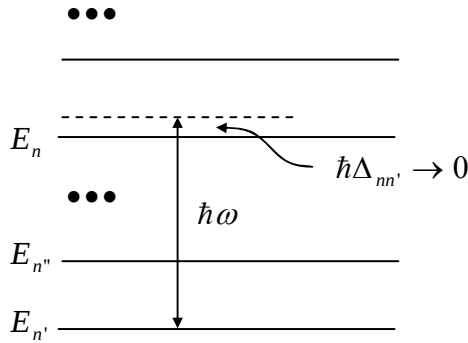


Fig. 6.10. Resonant excitation of one of the higher energy levels.

As a result, in this *two-level approximation* (that is of course not an approximation at all for two-level systems, such as spin- $\frac{1}{2}$ - see Sec. 5.1), we get a simple system of two linear equations:

$$\begin{aligned} i\hbar\dot{a}_n &= a_{n'} A e^{-i\Delta t}, \\ i\hbar\dot{a}_{n'} &= a_n A^* e^{+i\Delta t}, \end{aligned} \quad (6.94)$$

³⁰ Strictly speaking, another condition is that the number of “resonant” levels is also not too high – see Sec. 6.

³¹ The notion of detuning is also very useful in the classical theory of oscillations – see, e.g., CM Chapter 4.

³² Such omission of non-resonant terms is usually called the *Rotating Wave Approximation* (RWA); it is very instrumental not only in quantum mechanics, but also in the classical theory of oscillations - see, e.g., CM Secs. 4.3-4.5.

where I have used shorthand notation $A \equiv A_{nn'}$ and $\Delta \equiv \Delta_{nn'}$ - and will use it for a while - until other energy levels become involved (in the beginning of the next section). This system of linear differential equations may be solved exactly by the introduction of a new variable (for one of the levels only!)

$$b_n \equiv a_n e^{+i\Delta t}. \quad (6.95)$$

According to this formula,

$$a_n = b_n e^{-i\Delta t}, \quad \dot{a}_n = (\dot{b}_n - i\Delta b_n) e^{-i\Delta t}. \quad (6.96)$$

Plugging these relations into Eq. (94), we see that both equations of the system loose their explicit time dependence:

$$i\hbar(\dot{b}_n - i\Delta b_n) = a_n A, \quad i\hbar \dot{a}_n = b_n A^*, \quad (6.97)$$

and now may be readily solved by regular methods. For example, we may differentiate the first equation, and then use the second one to eliminate variable a_n :

$$i\hbar(\ddot{b}_n - i\Delta \dot{b}_n) = \dot{a}_n A = \frac{b_n A^*}{i\hbar} A = b_n \frac{|A|^2}{i\hbar}. \quad (6.98)$$

From mathematics we know that the resulting linear, second-order differential equation, with time-independent coefficients, has the following general solution,

$$b_n(t) = b_+ e^{\lambda_+ t} + b_- e^{\lambda_- t}, \quad (6.99)$$

whose characteristic exponents λ may be readily found by plugging any of the exponential functions into Eq. (98). In our case, both roots of the resulting characteristic equation,

$$\lambda^2 - i\Delta\lambda + \frac{|A|^2}{\hbar^2} = 0, \quad (6.100)$$

are purely imaginary: $\lambda_{\pm} = i(\Delta/2 \pm \Omega)$, where

Rabi
oscillations'
(half-)
frequency

$$\Omega \equiv \left(\frac{\Delta^2}{4} + \frac{|A|^2}{\hbar^2} \right)^{1/2}. \quad (6.101)$$

The coefficients $b_{\pm}$ are determined by initial conditions. If, as before, the system was completely on level n' initially, i.e. $a_n(0) = 1$, $a_n(0) = b_n(0) = 0$; then Eq. (99) immediately yields $b_- = -b_+$, so that

$$b_n(t) = 2ib_+ e^{i\Delta t/2} \sin \Omega t, \quad a_n(t) = 2ib_+ e^{-i\Delta t/2} \sin \Omega t, \quad \dot{a}_n(0) = 2ib_+ \Omega. \quad (6.102)$$

Now the coefficient b_+ may be readily found from the comparison of the last equality in Eq. (102) with the first of Eqs. (94), taken for $t = 0$, when $a_n = 1$. This comparison yields $2ib_+ \Omega = A/i\hbar$, and hence

$$a_n(t) = -\frac{A}{\hbar\Omega} e^{-i\Delta t/2} \sin \Omega t, \quad (6.103)$$

so that the n^{th} level occupancy is

$$W_n = |a_n|^2 = \frac{|A|^2}{\hbar^2 \Omega^2} \sin^2 \Omega t = \frac{|A|^2}{|A|^2 + (\hbar \Delta / 2)^2} \sin^2 \Omega t. \quad (6.104) \quad \text{Rabi formula}$$

This is the famous *Rabi formula*.³³ It shows that an increase of the perturbation amplitude $|A|$ leads not only to an increase of the amplitude of the probability oscillations, but also of their frequency 2Ω described by Eq. (101) – see Fig. 11.

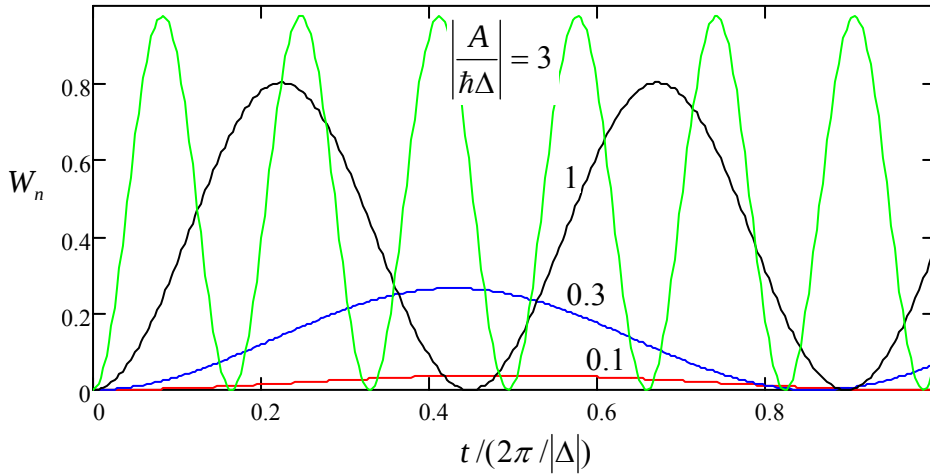


Fig. 6.11. Rabi oscillations.

Ultimately, at $|A| \gg \hbar|\Delta|$ (for example, at the exact resonance, $\Delta = 0$) Eqs. (101)-(102) give $\Omega = |A|/\hbar$ and $(W_n)_{\max} = 1$, i.e. describe a periodic, full “repumping” of the system from one level to another and back, with a frequency proportional to the perturbation amplitude. This effect gives a very convenient tool for manipulating two-level-systems (qubits, in the quantum information context). For example, limiting the external excitation time to $\Delta t = \pi/2\Omega$ (or an odd number of such intervals) we may completely transfer the system from one eigenstate (say, $\downarrow$) to the opposite one ($\uparrow$).³⁴ On the Bloch sphere (Fig. 5.1), this transfer corresponds to the representing point’s drive from the South Pole to the North Pole.

Note, however, that according to Eq. (90), if the system has energy levels other than n and n' , they also become occupied to some extent. Since the sum of occupancies should be 1, this means that $(W_n)_{\max}$ may approach 1 only if the excitation amplitude is very small, and hence the state switching time $\Delta t = \pi/2\Omega = \pi\hbar/2|A|$ is very long. The ultimate limit in this sense is provided by the harmonic oscillator where all energy levels are equidistant, and probability repumping between all of them occurs with the same rate. Hence, in that particular system, the implementation of the full Rabi oscillations is impossible even at the exact resonance.³⁵ In the opposite limit, when the detuning is large in comparison with $|A|/\hbar$, though still small in the sense of Eq. (93), the frequency of Rabi oscillations is completely determined by the detuning, and their amplitude is small:

³³ It was derived in 1952 by I. Rabi, in the context of his group’s pioneering experiments with microwave excitation of quantum states, using molecular beams in vacuum.

³⁴ In the quantum information science language, this is just a logic operation NOT performed on a single qubit.

³⁵ We, of course, already know what happens to the ground state of an oscillator at its external sinusoidal (or any other) excitation: it turns into the Glauber state, i.e. a superposition of *all* Fock states – see Sec. 5.5.

$$W_n(t) = 4 \frac{|A|^2}{\hbar^2 \Delta^2} \sin^2 \frac{\Delta t}{2} \ll 1, \quad \text{for } |A|^2 \ll (\hbar \Delta)^2. \quad (6.105)$$

However, I would not like these quantitative details to obscure from the reader the most important qualitative (OK, maybe semi-quantitative :-) conclusion of this section's analysis: the resonant increase of interlevel transition intensity at $\omega \rightarrow \omega_{nn'}$. Using the fundamental *Kramer-Kronig dispersion relations*,³⁶ based essentially only on very general causality arguments, it is easy to show (and hence left for reader's exercise) that in a medium incorporating many similar quantum systems (e.g., atoms or molecules), this increase of quantum transitions is accompanied by a sharp increase of external field's *absorption*. This effect has numerous practical applications including systems based on the electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopies, which are broadly used in material science, chemistry, and medicine. Unfortunately, I will not have time to discuss the related technical issues (in particular, interesting pulsing spectroscopy techniques) in detail, and have to refer the reader to special literature.³⁷

6.6. Quantum-mechanical Golden Rule

The last result of the past section, Eq. (105), may be used to derive one of the most important results of quantum mechanics – its so-called *Golden Rule*. For that, let us consider the case when the perturbation causes quantum transitions from a *discrete* energy level $E_{n'}$ into a group of eigenstates E_n with a dense (virtually continuous) spectrum – see Fig. 12a. If, for all states n of the group, the following conditions are satisfied

$$|A_{nn'}|^2 \ll (\hbar \Delta_{nn'})^2 \ll (\hbar \omega_{nn'})^2, \quad (6.106)$$

then Eq. (105) coincides with the result that would follow from Eq. (90). This means that we may apply Eq. (105), with indices n and n' duly restored, to any level n of our tight group. As a result, the total probability of having our system transferred from level n' to that group is

$$W_\Sigma(t) = \sum_n W_n(t) = \frac{4}{\hbar^2} \sum_n \frac{|A_{nn'}|^2}{\Delta_{nn'}^2} \sin^2 \frac{\Delta_{nn'} t}{2}. \quad (6.107)$$

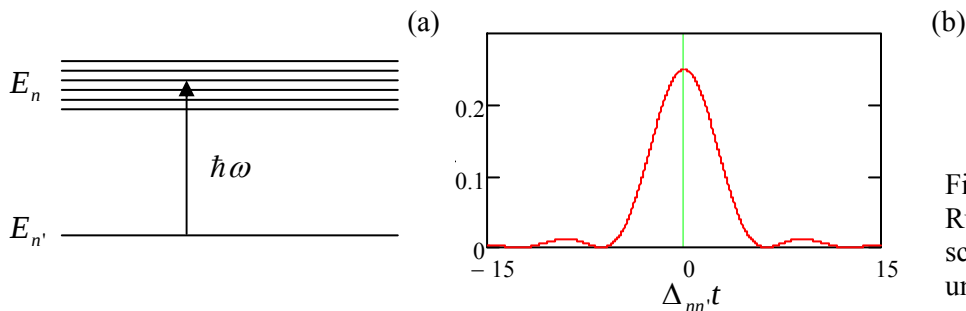


Fig. 6.12. Deriving the Golden Rule: (a) the energy level scheme, and (b) the function under integral (108).

³⁶ See, e.g., EM Sec. 7.3, in particular, the correspondence between Eqs. (7.55) and (7.56).

³⁷ For introductions see, e.g., J. Wertz and J. Bolton, *Electron Spin Resonance*, 2nd ed., Wiley, 2007; J. Keeler, *Understanding NMR Spectroscopy*, 2nd ed., Wiley, 2010.

Now comes the main, absolutely beautiful trick: let us assume that the summation over n will be limited to a tight group of very similar states for which the matrix elements $A_{nn'}$ are virtually similar (we will check the validity of this assumption later on), so that we can take it out of the sum (107) and then replace the sum with the corresponding integral:

$$W_{\Sigma}(t) = \frac{4|A_{nn'}|^2}{\hbar^2} \int \frac{1}{\Delta_{nn'}^2} \sin^2 \frac{\Delta_{nn'} t}{2} dn = \frac{4|A_{nn'}|^2 \rho_n t}{\hbar} \int \frac{1}{(\Delta_{nn'} t)^2} \sin^2 \left(\frac{\Delta_{nn'} t}{2} \right) d(-\Delta_{nn'} t), \quad (6.108)$$

where ρ_n is the density of eigenstates n on the energy axis:

$$\rho_n \equiv \frac{dn}{dE_n}. \quad (6.109) \quad \text{Density of states}$$

This density, as well as the matrix element $A_{nn'}$, have to be evaluated at $\Delta_{nn'} = 0$, i.e. at energy $E_n = E_{n'} + \hbar\omega$, and are assumed to be constant within the finite state group. At fixed E_n , the function under integral (108) is even and decreases fast at $|\Delta_{nn'} t| \gg 1$ – see Fig. 12b. Hence we may introduce a dimensionless integration variable $\xi \equiv \Delta_{nn'} t$, and extend integration over this variable formally from $-\infty$ to $+\infty$. Then Eq. (108) is reduced to a table integral,³⁸ and yields

$$W_{\Sigma}(t) = \frac{4|A_{nn'}|^2 \rho_n t}{\hbar} \int_{-\infty}^{+\infty} \frac{1}{\xi^2} \sin^2 \frac{\xi}{2} d\xi = \frac{4|A_{nn'}|^2 \rho_n t}{\hbar} \frac{\pi}{2} \equiv \Gamma t, \quad (6.110)$$

where constant

$$\Gamma = \frac{2\pi}{\hbar} |A_{nn'}|^2 \rho_n. \quad (6.111) \quad \text{Golden Rule of quantum mechanics}$$

is the called the *transition rate*.³⁹

This is one of the most famous and useful results of quantum mechanics, its *Golden Rule* (sometimes, rather unfairly, called the “Fermi Golden Rule”⁴⁰), which deserves much discussion. First of all, let us reproduce the reasoning already used in Sec. 2.5 to show that the meaning of rate Γ is much deeper than Eq. (110) seems to imply. Indeed, due to the conservation of the total probability, $W_{n'} + W_{\Sigma} = 1$, we can rewrite that equation as

$$\dot{W}_{n'}|_{t=0} = -\Gamma. \quad (6.112)$$

Evidently, this result cannot be true for $t \rightarrow \infty$, otherwise probability $W_{n'}$ would become negative. The reason for that apparent contradiction is that result (110) was obtained in the assumption that initially the system was completely on level n' : $W_{n'}(0) = 1$. Now, if in the initial moment the value of $W_{n'}$ is

³⁸ See, e.g., MA Eq. (6.12).

³⁹ In some texts, the density of states in Eq. (111) is replaced with expression $\sum_n \delta(E_n - E_{n'} - \hbar\omega)$. Indeed, the integration of this expression over any finite energy interval ΔE_n gives the same result $\Delta n = (dn/dE_n) \Delta E_n = \rho_n \Delta E_n$ as Eq. (111). Such replacement may be useful in some cases, but should be used with utmost care, and for most applications the more explicit form (111) is preferable.

⁴⁰ Actually, this result was developed mostly by the same P. A. M. Dirac in 1927; E. Fermi’s role was not much more than advertising it, under the name of “Golden Rule No. 2”, in his lecture notes on nuclear physics, which were published much later, in 1950. (To be fair to Fermi, he has never tried to pose as the Golden Rule’s author.)

different, result (110) has to be multiplied by that number, due to the linear relation (88) between da_n/dt and $a_{n'}$. Hence, instead of Eq. (112) we get a differential equation similar to Eq. (2.159),

$$\dot{W}_{n'} = -\Gamma W_{n'}, \quad (6.113)$$

which, for time-independent Γ , has the evident solution,

$$W_{n'}(t) = W_{n'}(0)e^{-\Gamma t}, \quad (6.114)$$

describing an exponential decay of the initial state's occupancy, with time constant $\tau = 1/\Gamma$.

I would ask the reader to think again about this fascinating mathematical result: by summation of *periodic oscillations* (105) over many levels n , we have got an *exponential evolution* (114) of the probability. The main trick here is of course that the effective range ΔE of states E_n , giving the dominating contribution into integral (108), shrinks with time: $\Delta E_n \sim \hbar/t$.⁴¹ By the way, since most of the decay takes place at times $t \sim \tau \equiv 1/\Gamma$, the range of participating final energies may be estimated as

$$\Delta E_n \sim \frac{\hbar}{\tau} = \hbar\Gamma. \quad (6.115)$$

This estimate is very instrumental for the formulation of conditions of validity of the Golden Rule (111). First, we have assumed that the matrix elements of the perturbation and the density of states do not depend on energy within interval (115). This gives the following requirement

$$\Delta E_n \sim \hbar\Gamma \ll E_n - E_{n'} \sim \hbar\omega, \quad (6.116)$$

Second, for the transfer from sum (107) to integral (108), we need the number of states within that energy interval, $\Delta N_n = \rho_n \Delta E_n$, to be much larger than 1. Merging Eq. (116) with Eq. (93) for all energy levels $n'' \neq n, n'$ not participating in the resonant transfer, we may summarize all conditions of the Golden Rule validity as

$$\rho_n^{-1} \ll \hbar\Gamma \ll \hbar|\omega \pm \omega_{n'n''}|. \quad (6.117)$$

(The reader may ask whether I have forgotten the condition expressed by the first of Eqs. (106). However, for $\Delta_{nn'} \sim \Delta E_n/\hbar \sim \Gamma$, this condition is just $|A_{nn'}|^2 \ll (\hbar\Gamma)^2$, so that plugging it into Eq. (111),

$$\Gamma \ll \frac{2\pi}{\hbar} (\hbar\Gamma)^2 \rho_n, \quad (6.118)$$

and canceling one Γ and one $\hbar$, we see that this requirement coincides with the left relation in Eq. (117) above.)

Let us have a look at whether these conditions may be satisfied in practice, at least in some cases. For example, let us consider the optical ionization of an atom, with the released electron confined in a volume of the order of $1 \text{ cm}^3 = 10^{-6} \text{ m}^3$. According to Eq. (1.82), with E of the order of the atomic ionization energy $E_n - E_m = \hbar\omega \sim 1 \text{ eV}$, the density of electron states in that volume is of the order of 10^{17} 1/eV . Thus conditions (117) provide an approximately 15-orders-of-magnitude range for acceptable

⁴¹ Here we have run again, in a more general context, into the “energy-time uncertainty relation” which was already discussed in the end of Sec. 2.5. Let me advise the reader to revisit that important discussion.

values of $\hbar\Gamma$. This illustration should give the reader a taste of why the Golden Rules is applicable to so many situations.

Finally, the physical picture of initial state's decay (which will also be the key for our discussion of quantum mechanics of “open” systems in the next chapter) is also very important. According to Eq. (114), the external excitation transfers the system onto the continuous spectrum of levels n , and it never comes back on the initial level n' . However, it was derived from quantum mechanics of Hamiltonian systems, whose equations are invariant with respect to time reversal. This paradox is a result of the generalization (113) of the exact result (112), that breaks the time reversal symmetry, but is absolutely adequate for the physics under study. Some gut feeling of the physical sense of this irreversibility may be obtained from the following observation. From our wave-mechanics experience, we know that the distance between adjacent orbital energy levels tends to zero only if the system size goes to infinity. This means that the assumption of continuous energy spectrum of finite states n essentially requires these states to be infinitely extended in space – essentially being free de Broglie waves. The Golden Rule approach corresponds to the (physically justified) assumption that in an infinitely large system the traveling waves excited by a local source and propagating outward from it, would never come back, and even if they do, the unpredictable phase shifts introduced by the uncontrollable perturbations on their way would never allow them to sum up in the way necessary to bring the system back into the initial state n' .⁴²

Maybe the best illustration of this interpretation is given by the following problem - which is a toy model of the photoelectric effect that was briefly discussed in Sec. 1.1(iii). A 1D particle is initially trapped in the ground state of a narrow quantum well,

$$U(x) = -w\delta(x). \quad (6.119)$$

Let us use the Golden Rule to find rate Γ of particle's “ionization” (i.e. its excitation into an extended, delocalized state) by a weak classical sinusoidal force of amplitude F_0 and frequency ω . As a reminder, finding the initial, localized state (n') of such particle was the task of Problem 2.14, and its solution was

$$\psi_{n'}(x) = \kappa^{1/2} \exp\{-\kappa|x|\}, \quad \kappa \equiv \frac{m\omega}{\hbar^2}, \quad E_{n'} = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{m\omega^2}{2\hbar^2}. \quad (6.120)$$

Extended states n with continuous spectrum, for this problem exist only at energies $E_n > 0$, so that the excitation rate is different from zero only for frequencies

$$\omega > \omega_t \equiv \frac{|E_{n'}|}{\hbar} = \frac{m\omega^2}{2\hbar^3}. \quad (6.121)$$

The weak sinusoidal force may be described by the following perturbation Hamiltonian,

$$\hat{H}^{(1)} = -F(t)\hat{x} = -F_0\hat{x}\cos\omega t = -\frac{F_0}{2}\hat{x}\left(e^{i\omega t} + e^{-i\omega t}\right), \quad \text{for } t > 0, \quad (6.122)$$

so that according to Eq. (86), that serves as the amplitude operator definition, in this case

⁴² This situation is very much similar to the entropy increase in macroscopic systems, which is postulated in thermodynamics, and justified in statistical physics, even though it is based on time-reversible laws of mechanics – see, e.g., SM Sec. 1.2 and Sec. 2.2.

$$\hat{A} = \hat{A}^\dagger = -\frac{F_0}{2} \hat{x}. \quad (6.123)$$

Now the matrix elements $A_{nn'}$ that participate in Eq. (111) may be calculated in the coordinate representation:

$$A_{nn'} = \int_{-\infty}^{+\infty} \psi_n^*(x) \hat{A}(x) \psi_{n'}(x) dx = -\frac{F_0}{2} \int_{-\infty}^{+\infty} \psi_n^*(x) x \psi_{n'}(x) dx. \quad (6.124)$$

Since, according to Eq. (120), the initial $\psi_{n'}$ is a *symmetric* function of x , a nonvanishing contribution to this integral is given only by *asymmetric* functions $\psi_n(x)$, proportional to $\sin k_n x$, with wavenumber k_n related to the final energy by the well-familiar equality (1.77):

$$\frac{\hbar^2 k_n^2}{2m} = E_n. \quad (6.125)$$

As we know from Sec. 2.5 (see in particular Eq. (2.124) and its discussion), such asymmetric functions, with $\psi_n(0) = 0$, are not affected by the zero-centered delta-functional potential (119), and their density ρ_n is the same as in a completely free space, and we can use Eq. (1.94). (Actually, since that relation was derived for traveling waves, it is more prudent to repeat the calculation that has led to that result, confining the waves on an artificial segment $[-l/2, +l/2]$ - so long,

$$k_n l, \kappa l \gg 1, \quad (6.126)$$

that it does not affect the initial localized state and the excitation process. Then the confinement requirement $\psi_n(\pm l/2) = 0$ immediately yields the condition $k_n l/2 = n\pi$, so that Eq. (1.94) is indeed valid, but only for positive values of k_n , because $\sin k_n x$ with $k_n \rightarrow -k_n$ does not give an independent standing-wave eigenstate.) Hence the finite state density is

$$\rho_n \equiv \frac{dn}{dE_n} = \frac{dn}{dk_n} / \frac{dE_n}{dk_n} = \frac{l}{2\pi} / \frac{\hbar^2 k_n}{m} = \frac{lm}{2\pi \hbar^2 k_n}. \quad (6.127)$$

It may look troubling that the density of states depends on artificial segment's length l , but the same l also participates in the final wavefunction normalization factor,⁴³

$$\psi_n = \left(\frac{2}{l}\right)^{1/2} \sin k_n x, \quad (6.128)$$

and hence the matrix element (124):

$$A_{nn'} = -\frac{F_0}{2} \left(\frac{2\kappa}{l}\right)^{1/2} \int_{-l}^{+l} \sin k_n x e^{-\kappa|x|} x dx = -\frac{F_0}{2i} \left(\frac{2\kappa}{l}\right)^{1/2} \left(\int_0^l e^{(ik_n - \kappa)x} x dx - \int_0^l e^{-(ik_n + \kappa)x} x dx \right). \quad (6.129)$$

These two integrals may be readily worked out by parts. Taking into account that, according to condition (126), their upper limits may be extended to ∞ , the result is

⁴³ The normalization to infinite volume, using Eq. (5.55), is also possible, but less convenient in such problems.

$$A_{nn'} = -\left(\frac{2\kappa}{l}\right)^{1/2} F_0 \frac{2k_n\kappa}{(k_n^2 + \kappa^2)^2}, \quad (6.130)$$

so that finally we get an expression for the rate, which is independent of the artificially introduced l :

$$\Gamma = \frac{2\pi}{\hbar} |A_{nn'}|^2 \rho_n = \frac{2\pi}{\hbar} \left[\left(\frac{2\kappa}{l}\right)^{1/2} F_0 \frac{2k_n\kappa}{(k_n^2 + \kappa^2)^2} \right]^2 \frac{lm}{2\pi\hbar^2 k_n} = \frac{8F_0^2 m k_n \kappa^3}{\hbar^3 (k_n^2 + \kappa^2)^4}. \quad (6.131)$$

Note that due to the above definitions of k_n and κ , the expression in parentheses in the denominator of the last formula does not depend on the quantum well parameter W , and is a function of only the excitation frequency ω (and particle's mass):

$$\frac{\hbar^2 (k_n^2 + \kappa^2)}{2m} = E_n - E_{n'} = \hbar\omega. \quad (6.132)$$

As a result, Eq. (131) may be recast simply as

$$\hbar\Gamma = \frac{F_0^2 \omega^3 k_n}{2(\hbar\omega)^4}. \quad (6.133)$$

What is still hidden here is that k_n , defined by to Eq. (125) with $E_n = E_{n'} + \hbar\omega$, is a function of frequency, changing as $\omega^{1/2}$ at $\omega \gg \omega_t$ (so that Γ drops as $\omega^{-7/2}$ at $\omega \rightarrow \infty$), and as $(\omega - \omega_t)^{1/2}$ when ω approaches the “red boundary” $\omega_t \equiv |E_{n'}|/\hbar = m\omega^2/2\hbar^3$ of the ionization effect, so that $\Gamma \propto (\omega - \omega_t)^{1/2} \rightarrow 0$ in that limit as well. We see that our toy model does describe this main feature of the photoelectric effect, whose explanation by Einstein was essentially the starting point of quantum mechanics - see Sec. 1.1. The (very similar) analysis of this effect in a more realistic model, the hydrogen atom's ionization, is left for reader's exercise.

6.7. Golden Rule for step-like perturbations

Now let us reuse some of our results for a perturbation being turned on at $t = 0$, but after that time-independent:

$$\hat{H}^{(1)}(t) = \begin{cases} 0, & t < 0, \\ \hat{H}^{(1)} = \text{const}, & t \geq 0. \end{cases} \quad (6.134) \quad \text{Step-like perturbation}$$

A superficial comparison of this equation and our former Eq. (69) seems to indicate that we may use all our previous results, taking $\omega = 0$. However, that conclusion does not take into account the fact that analyzing both the two-level approximation and the Golden Rule for continuous spectrum, we have neglected the second (non-resonant) term in Eq. (90). This why it is more prudent to use the general Eq. (86),

$$i\hbar\dot{a}_n = \sum_{n'} a_{n'} H^{(1)}_{nn'} e^{i\omega_{nn'}t}, \quad (6.135)$$

in which the matrix element of the perturbation is now time-independent. We see that it is formally equivalent to Eq. (88) with only the first (resonant) term kept, if we make the following replacements:

$$\hat{A} \rightarrow \hat{H}^{(1)}, \quad \Delta_{nn'} \equiv \omega - \omega_{nn'} \rightarrow -\omega_{nn'}. \quad (6.136)$$

As a sanity check, let us revisit a two-level system such as two quantum wells coupled by tunneling – see Fig. 13a. It is convenient to include the energy difference $E_n - E_{n'}$ between the two levels into the unperturbed Hamiltonian, so that perturbation (134) describes only the localized state coupling due to tunneling through the energy barrier separating the wells. (The turning on of the coupling, described by Eq. (134), may be achieved, for example, by a rapid lowering of the barrier at $t = 0$.) Then, after replacements (136), we are getting an analog of Eq. (104):

$$W_n = |a_n|^2 = \frac{|H_{nn'}^{(1)}|^2}{\hbar^2 \Omega^2} \sin^2 \Omega t, \quad (6.137)$$

where frequency Ω of the periodic “probability repumping” between levels n' and n is now described, instead of Eq. (104), by relation

$$2\Omega = \left(\omega_{nn'}^2 + 4 \frac{|H_{nn'}^{(1)}|^2}{\hbar^2} \right)^{1/2} = \frac{1}{\hbar} \left[(E_n - E_{n'})^2 + 4 H_{nn'}^{(1)} H_{n'n}^{(1)} \right]^{1/2}. \quad (6.138)$$

But these are exactly the quantum oscillations that have already been discussed in Sec. 2.6 – now derived for an arbitrary quantum wells and tunnel barrier shape.

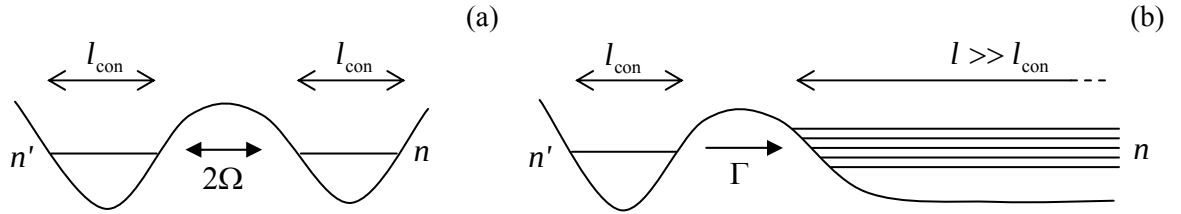


Fig. 6.13. Quantum-well implementation of coupling of a discrete-energy state n' to (a) another discrete-energy state, and (b) a state continuum, due to tunneling through a potential barrier.

The similarity of Eqs. (104) and (137) shows that the Rabi oscillations and the “usual” quantum oscillations have essentially the same physical nature, besides that in the former case the external rf signal quantum $\hbar\omega$ bridges over the state energy difference. We may also compare result (138) with our analysis of a two-level system, with a similar time-independent perturbation, in Sec. 1. According to Eq. (29), its eigenenergies differ by

$$E_+ - E_- = \left[(H_{11} - H_{22})^2 + 4H_{12}H_{21} \right]^{1/2}. \quad (6.139)$$

But this is exactly the result given by Eq. (138), provided that we consider $(H_{11} - H_{22})$ as the difference $(E_n - E_{n'})$ of unperturbed state energies rather than as a perturbation, as we certainly have a right to do.

Now let us consider the effect of perturbation (134) in the case when it creates coupling between the initial (discrete) energy level and a dense group of states with a quasi-continuum spectrum, in the same energy range. Figure 13b shows an example of such a system: a quantum well separated by a

penetrable tunnel barrier from an extended region with a quasi-continuous energy spectrum. Making replacements (136) in Eq. (111), we may present the Golden Rule for this case as

$$\Gamma = \frac{2\pi}{\hbar} |H_{nn'}^{(1)}|^2 \rho_n, \quad (6.140)$$

where states n and n' now have the same energy.⁴⁴

It is very informative to compare this result with Eq. (138) for a symmetric ($E_n = E_{n'}$) double quantum well using the same tunnel barrier – see Fig. 13. For the latter case, Eq. (138) yields

$$\Omega = \frac{1}{\hbar} |H_{nn'}^{(1)}|_{\text{con}}. \quad (6.141)$$

Here I have used index “con” (from “confinement”) to emphasize that this matrix element is rather different from the one participating in Eq. (140). Indeed, in the latter case, the matrix element,

$$H_{nn'}^{(1)} = \langle n | \hat{H}^{(1)} | n' \rangle = \int \psi_n^* \hat{H}^{(1)} \psi_{n'} dx, \quad (6.142)$$

has to be calculated for two similar wavefunctions ψ_n and $\psi_{n'}$ confined to spatial intervals of the same scale l_{con} , while in Eq. (140), wavefunctions ψ_n are extended to a much larger distance $l \gg l_{\text{con}}$ – see Fig. 13. As Eq. (129) tells us, in the 1D model we are considering now, this means an additional factor small factor of the order of $(l_{\text{con}}/l)^{1/2}$. Now using Eq. (128) as a crude but suitable model for the finite-state wavefunctions, we arrive at the following estimate:

$$\hbar\Gamma \sim 2\pi |H_{nn'}^{(1)}|_{\text{con}}^2 \frac{l_{\text{con}}}{l} \rho_n \sim 2\pi |H_{nn'}^{(1)}|_{\text{con}}^2 \frac{l_{\text{con}}}{l} \frac{lm}{2\pi\hbar^2 k_n} \sim \frac{|H_{nn'}^{(1)}|_{\text{con}}^2}{\Delta E_{n'}} = \frac{(\hbar\Omega)^2}{\Delta E_{n'}}, \quad (6.143)$$

where $\Delta E_{n'} \sim \hbar^2/ml_{\text{con}}^2$ is the scale of the differences between eigenenergies of the particle in an unperturbed quantum well. Since the condition of validity of the perturbative formula (140) is $\hbar\Omega \ll \Delta E_{n'}$, we see that⁴⁵

$$\hbar\Gamma \sim \frac{\hbar\Omega}{\Delta E_m} \hbar\Omega \ll \hbar\Omega. \quad (6.144)$$

Hence the rate of (irreversible) quantum tunneling into continuum is always *much lower* than the frequency of (reversible) quantum oscillations between states separated with the same potential barrier – at least for the case when both are much lower than $\Delta E_{n'}/\hbar$, so that the perturbation theory is valid. A handwaving interpretation of this result is that the confined particle wanders beyond the barrier and back many times before finally “deciding” to perform an irreversible transition into unconfined continuum.⁴⁶

⁴⁴ The condition of its validity is again given by Eq. (117), but with $\omega \rightarrow 0$ in the upper limit.

⁴⁵ It is straightforward to show that in this form, the estimate is valid for a similar problem of any spatial dimensionality, not just the 1D case we have analyzed.

⁴⁶ This qualitative picture may be verified, for example, using the experimentally observable effects of dispersive electromagnetic environment on electron tunneling - see P. Delsing *et al.*, *Phys. Rev. Lett.* **63**, 1180 (1989).

Let me conclude this section (and this chapter) with the application of Eq. (140) to an important case, which will provide us with a smooth transition to the next chapter's topics. Consider a *composite* system consisting of two parts, a and b , with the energy spectra sketched in Fig. 14.

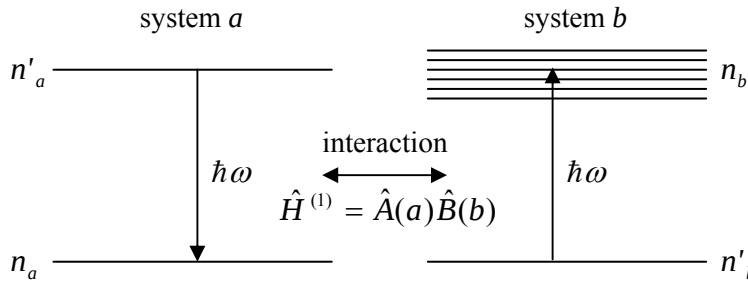


Fig. 6.14. Energy relaxation in system a due to its coupling with system b (which serves as the environment of a).

Let the systems be completely independent initially. The independence means that in the absence of perturbation, the total Hamiltonian of the system at $t < 0$ may be presented as a sum

$$\hat{H}^{(0)} = \hat{H}_a(a) + \hat{H}_b(b), \quad (6.145)$$

where arguments a and b symbolize the non-overlapping sets of variables of the two systems. Then eigenkets of the system may be naturally factored as⁴⁷

$$|n\rangle = |n_a\rangle \otimes |n_b\rangle, \quad (6.146)$$

while its eigenenergies separate into a sum, just as the Hamiltonian (145) does:

$$\begin{aligned} \hat{H}^{(0)}|n\rangle &= (\hat{H}_a + \hat{H}_b)|n_a\rangle \otimes |n_b\rangle = (\hat{H}_a|n_a\rangle) \otimes |n_b\rangle + (\hat{H}_b|n_b\rangle) \otimes |n_a\rangle \\ &= (E_{na}|n_a\rangle) \otimes |n_b\rangle + (E_{nb}|n_b\rangle) \otimes |n_a\rangle = (E_{na} + E_{nb})|n\rangle. \end{aligned} \quad (6.147)$$

Analysis of such a composite system is much easier when the interaction of its components may be presented as a product of two Hermitian operators, each depending only on the degrees of freedom of only one component system:

$$\hat{H}^{(1)} = \hat{A}(a)\hat{B}(b). \quad (6.148)$$

A typical example of such a *bilinear* interaction Hamiltonian is the electric-dipole interaction between an atomic-scale electron system (with a size of the order of the Bohr radius $r_B \sim 10^{-10}$ m) and the electromagnetic field at optical frequencies $\omega \sim 10^{16}$ s⁻¹, with wavelength $\lambda = 2\pi c/\omega \sim 10^{-6}$ m $\gg r_B$.⁴⁸

$$\hat{H}^{(1)} = -\hat{\mathbf{d}} \cdot \hat{\mathcal{E}}, \quad \text{with } \hat{\mathbf{d}} \equiv \sum_k q_k \hat{\mathbf{r}}_k, \quad (6.149)$$

where the dipole electric moment $\mathbf{d}$ depends only on positions $\mathbf{r}_k$ of charged particles (numbered with index k), while that of electric field $\mathcal{E}$ is a function of only the electromagnetic field's degrees of freedom – see Chapter 9 below.

⁴⁷ Sign $\otimes$ is used to denote the formation of a joint ket-vector from kets of independent systems (“belonging to different Hilbert spaces”). Evidently, the order of operands in such a “product” may be changed at will.

⁴⁸ See, e.g., EM Sec. 3.1, in particular Eq. (3.16), in which letter $\mathbf{p}$ is used for the electric dipole moment.

Returning to the general situation shown in Fig. 14, if the component system a was initially in an excited state n'_a , interaction (148) may bring it to another discrete state n_a of a lower energy - for example, the ground state. In the process of this transition, the released energy, in the form of energy quantum

$$\hbar\omega \equiv E_{n'_a} - E_{n_a}, \quad (6.150)$$

is picked up by system b :

$$E_{nb} - E_{n'_b} = \hbar\omega. \quad (6.151)$$

(In typical applications, though not always, the initial state n'_b of that system is its ground state.) If the finite state n_b of the system is inside a state group with quasi-continuous energy spectrum (Fig. 14), the process has the exponential character (114)⁴⁹ and may be interpreted as the effect of *energy relaxation* of system a , with the released energy quantum $\hbar\omega$ absorbed by system b . Note that since the quasi-continuous spectrum essentially requires a system of large spatial size, such model is very convenient for description of the *environment* of system a . (In physics, the “environment” typically means all the Universe less the system under consideration.)

The relaxation rate Γ may be described by the Golden Rule. Since perturbation (148) does not depend on time explicitly, and the total energy of the composite system does not change, we may use Eq. (140) that, with the account of Eqs. (146) and (148), takes the form

$$\Gamma = \frac{2\pi}{\hbar} |A_{nn'}|^2 |B_{nn'}|^2 \rho_n, \quad \text{where } A_{nn'} \equiv \langle n_a | \hat{A} | n'_a \rangle, B_{nn'} = \langle n_b | \hat{B} | n'_b \rangle, \quad (6.152)$$

Golden
Rule
for coupled
systems

with ρ_n being the density of states of the finite states of system b , at the relevant energy $E_{nb} = E_{n'_b} + \hbar\omega = E_{n'_b} + (E_{n'_a} - E_{n_a})$. In particular, Eq. (152), with the dipole Hamiltonian (149), enables a very simple calculation of the natural linewidth of atomic electric dipole transitions. However, such calculation has to be postponed until Chapter 9 in which we will discuss the electromagnetic field quantization - i.e., the exact nature of states n_b and n'_b for this problem. Instead, I will proceed to a discussion of the effects of interaction of quantum systems with their environment, toward which the situation shown in Fig. 14 provides a clear path.

6.8. Exercise problems

6.1. Use Eq. (13) to prove the Hellmann-Feynman theorem:⁵⁰

$$\frac{\partial E_n}{\partial \lambda} = \langle n | \frac{\partial \hat{H}}{\partial \lambda} | n \rangle,$$

where λ is an arbitrary c -number parameter, and then use this theorem to prove the first of Eqs. (3.201).

6.2. Analyze the relation between Eq. (15) and the results of classical analysis⁵¹ of a similar anharmonic (“nonlinear”) oscillator.

⁴⁹ The process is evidently *spontaneous*, i.e. does not require any external agent, and starts as soon as either the interaction (127) has been turned on, or (if it is always on) as soon as system a is placed into the excited state n'_a .

⁵⁰ As a reminder, its proof for the particular case of wave mechanics was the subject of Problem 1.4.

6.3. A weak additional force F is applied to a 1D particle that was placed into a hard-wall quantum well with

$$U(x) = \begin{cases} 0, & \text{for } 0 < x < a, \\ +\infty, & \text{otherwise.} \end{cases}$$

Calculate, sketch, and discuss the first-order perturbation of its ground-state wavefunction.

6.4. A 2D quantum particle is confined in a square-shaped quantum well with infinitely high walls and slightly skewed floor:

$$U = \begin{cases} \mu xy, & \text{for } 0 < x < L \text{ and } 0 < y < L, \\ +\infty, & \text{otherwise.} \end{cases}$$

In the first order in the small parameter μ , find energies of the ground state and the lowest excited state of the system. Formulate the conditions of validity of your result.

Hint: To save reader's time on a straightforward but longish integration by parts, I can offer the following integral:

$$\int_0^1 \sin(\pi\xi) \sin(2\pi\xi) \xi d\xi = -\frac{8}{9\pi^2}.$$

6.5. Calculate the lowest-order relativistic correction to the ground-state energy of a 1D harmonic oscillator.

6.6. A 1D particle of mass m is localized at a narrow potential well which may be approximated with a delta-function:

$$U(x) = -w\delta(x), \quad \text{with } w > 0.$$

Calculate the change of its ground state energy by an additional weak, time-independent force F , in the first nonvanishing approximation of the perturbation theory. Discuss the limits of validity of this result, taking into account that at $F \neq 0$, the localized state of the particle is metastable.

6.7. Use the perturbation theory results to calculate the eigenvalues of the observable L^2 , in the limit $l \approx |m| \gg 1$, by purely wave-mechanical means.

Hint: Try the following substitution: $\Theta(\theta) = f(\theta)/\sin^{1/2}\theta$.

6.8. In the first nonvanishing order of the perturbation theory, calculate the shift of the ground-state energy of an electrically charged spherical rotator (i.e. a particle of mass m , free to move over a spherical surface of radius R) due to a weak, uniform, time-independent electric field $\mathcal{E}$.

6.9. Use the perturbation theory to evaluate the effect of a constant electric field $\mathbf{E}$ on the ground state energy E_g of a hydrogen atom. In particular:

⁵¹ See, e.g., CM Sec. 4.2.

- (i) calculate the 1st-order shift of E_g ,
- (ii) bring the expression for the 2nd-order shift (neglecting the extended unperturbed states with $E > 0$) to the simplest possible analytical form,
- (iii) find the lower and upper bounds on the result, and
- (iv) discuss the simplest manifestations of the shift (called the *quadratic Stark effect*).

6.10.* A particle of mass m , with electric charge q , is in its ground s-state with known energy $E_g < 0$, being localized by a very short-range, spherically-symmetric potential well. Calculate its electric polarizability α .

6.11. In the first nonvanishing order of the perturbation theory, calculate the correction to energies of the ground state and all lowest excited states of a hydrogen-like atom/ion, due to electron's penetration into its nucleus, modeling it as a spinless, uniformly charged sphere of radius $R \ll r_B/Z$.

6.12. A spin- $1/2$ particle is placed into a magnetic field

$$\mathcal{B} = \mathcal{B}_z \mathbf{n}_z + \mathcal{B}_x \mathbf{n}_x, \quad \text{with } |\mathcal{B}_x| \ll |\mathcal{B}_z|.$$

Calculate its energy levels:

- (i) exactly, and
- (ii) in the first nonvanishing order of the perturbation theory in small $\mathcal{B}_x$.

Compare the results of the two approaches.

6.13. Use the perturbation theory to analyze the orbital diamagnetism. Namely, calculate the magnetic susceptibility χ_m of a dilute gas due to the orbital motion of a single electron confined inside each gas particle.

Hint: You may like to use the well-known formula for the magnetic energy u per unit volume of a linear medium:

$$u = \mathcal{B}^2 / 2\mu,$$

where $\mathcal{B}$ is the applied magnetic field, and μ is the magnetic permeability, related to the susceptibility as $\mu \equiv \mu_0(1 + \chi_m)$.⁵²

6.14.* Analyze the statistics of the spacing $S \equiv E_+ - E_-$ between energy levels of a two-level system, assuming that all elements H_{ij} of its Hamiltonian matrix (6.27) are independent random numbers, with equal and constant probability densities within the energy interval of interest. Compare the result with that for a purely diagonal matrix, with the similar probability distribution of the diagonal elements.

6.15. Discuss how to calculate the energy level degeneracy lifting in the second order of the perturbation theory, assuming that it is not lifted in the first order. Carry out such a calculation for a plane rotator of mass m and radius R , carrying electric charge q , and placed into a weak, uniform, constant electric field $\mathcal{E}$.

⁵² See, e.g., EM Sec. 5.5, in particular Eqs. (5.127) and (5.112).

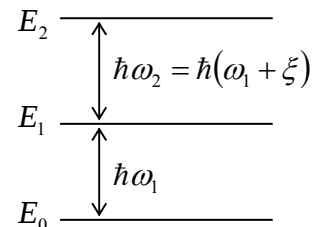
6.16. Use the single-particle approximation to find the complex dielectric constant $\epsilon(\omega)$ of a dilute gas of similar atoms, due to their induced electric polarization by a weak external ac field, for a field frequency ω very close to one of quantum transition frequencies ω_{mn} , defined by Eq. (85).

Hint: In the single-particle approximation, atom's response to an external field is described as that of Z similar, non-interacting electrons moving in an effective static attracting potential – generally induced not only by the nuclei but also by other electrons.

6.17. Use the solution of the previous problem to generalize the expression for the London dispersion force between two electroneutral molecules (whose calculation in the harmonic oscillator model was the subject of Problems 3.18 and 5.11) to the single-particle model with an arbitrary energy spectrum.

6.18. Use the solution of the previous problem to calculate the potential energy of interaction of two hydrogen atoms, both in their ground state, separated by distance $r \gg r_B$.

6.19. In a certain quantum system, distances between three lowest energy levels are slightly different - see Fig. on the right ($|\xi| \ll \omega_{1,2}$). Find the time necessary to populate the first excited level almost completely (with a given precision $\varepsilon \ll 1$), using the Rabi oscillation effect, if at $t = 0$ the system is completely in its ground state.



Hint: Assume that all matrix elements of the perturbation Hamiltonian are known, and are all proportional to the external rf field amplitude.

6.20. A weak external force pulse $F(t)$, of a finite time duration, is applied to a 1D harmonic oscillator that initially was in its ground state.

(i) Calculate, in the lowest nonvanishing order of the perturbation theory, the probability that the pulse drives the oscillator into an excited state.

(ii) Formulate the condition of validity of the result, and compare it with the exact solution of the problem.

(iii) Spell out the perturbative result for a Gaussian-shaped waveform,

$$F(t) = F_0 \exp\{-t^2 / \tau^2\},$$

and analyze its dependence on the effective duration τ of the pulse.

6.21. A charged plane rotator, initially in its ground state, is placed into a spatially-uniform, but time-dependent external field $\mathcal{E}(t)$, applied at $t = 0$.

(i) Calculate, in the lowest nonvanishing order in field's strength, the probability that the pulse drives the rotator oscillator into its n^{th} excited state.

(ii) Spell out and analyze your results for a rotating field.

(iii) Same for an ac field with fixed polarization.

6.22.

(i) Develop the general theory of excitations of the higher levels of a discrete-spectrum system, initially in the ground state, by a weak time-dependent perturbation, up to the 2nd order.

(ii) Apply the theory to the system analyzed in the previous problem (a plane rotator driven by a time-dependent electric field) to find out what excitations, forbidden in the 1st order of the perturbation theory, are allowed in its 2nd order.

6.23. A heavy, relativistic particle, with the electric charge $q = Ze$, passes by a hydrogen atom, initially in its ground state, with the impact parameter (shortest distance) b within the limits $r_B \ll b \ll r_B/\alpha$, where $\alpha \approx 1/137$ is the fine structure constant. Calculate the probability of atom's transition to its lowest excited states.

6.24.* A particle of mass m is initially in the localized ground state, with the known energy $E_g < 0$, of a very small, spherically-symmetric potential well. Calculate the rate of its delocalization ("ionization") by an applied force $\mathbf{F}(t) = \mathbf{n}_F F_0 \cos \omega t$, with a time-independent orientation $\mathbf{n}_F$, and discuss its dependence on frequency ω .

6.25.* Calculate the rate of ionization of a hydrogen atom, initially in its ground state, by a classical, linearly polarized electromagnetic wave with electric field's amplitude $\mathcal{E}_0$, and frequency ω within the range

$$\frac{\hbar}{m_e r_B^2} \ll \omega \ll \frac{c}{r_B},$$

where r_B is the Bohr radius. Recast your result in terms of the cross-section of this electromagnetic wave absorption process. Discuss semi-quantitatively what changes would be necessary in the theory if either of the above conditions had been violated.

6.26. For the system of two weakly coupled quantum wells (see Fig. 13a), write the system of differential equations for the probability amplitudes a_n defined by Eq. (2.199), and in particular prove Eqs. (2.201) - which were just guessed in Sec. 2.7.

6.27.* Use the quantum-mechanical Golden Rule to derive the general expression for the electric current I through a weak tunnel junction between two conductors, biased with dc voltage V , treating the conduction electrons as a Fermi gas, in which the electron-electron interaction is limited to the Pauli exclusion principle. Simplify the result in the low-voltage limit.

Hint: The electric current flowing through a weak tunnel junction is so low that its perturbation of the electron states inside each conductor is negligible.

6.28.* Generalize the result of the previous problem to the case when a weak tunnel junction is biased with voltage $V(t) = \bar{V} + A \cos \omega t$, with $\hbar \omega$ generally comparable with $e|\bar{V}|$ and eA .

6.29.* Use the quantum-mechanical Golden Rule to derive the Landau-Zener formula (2.266).

6.30. Calculate, in the 2nd order of the perturbation theory, the rate Γ of transitions between different states of a continuous group (of virtually the same energy E_n), induced by a monochromatic perturbation of frequency ω , with $\hbar\omega$ comparable to the distances between other, discrete levels of the system.

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Chapter 7. Open Quantum Systems

This chapter discusses the effects of interaction of a quantum system with its environment, and in particular, with the instruments used for measurements. Some part of this material is on the fine line between quantum mechanics and (quantum) statistical physics. Here I will only cover those aspects of this field which are of key importance for the basic goals of this course, in particular for the discussion of quantum measurements in the end of the chapter.¹

7.1. Open systems and the density matrix

All the way until the very end of the previous chapter, we have discussed quantum systems isolated from their environment. Indeed, from the very beginning we have assumed that we are dealing with the statistical ensembles of systems as similar to each other as only allowed by laws of quantum mechanics. Each member of such an ensemble, called *pure* or *coherent*, may be described by the same quantum state α - in the wave mechanics case, by the same wavefunction Ψ_α . Even our discussion of the Golden Rule in the end of the last chapter, in particular its form in which one component system (in Fig. 6.13, system b) may be used as a model of the environment of another component (a), was still based on the assumption of a pure initial state (6.146) of the system. Since the interaction of two component systems was described by a certain Hamiltonian (the one given by Eq. (6.145) for example), for the state α of the system as a whole at arbitrary instant we might write

$$|\alpha\rangle = \sum_n \alpha_n |n\rangle = \sum_n \alpha_n |n_a\rangle \otimes |n_b\rangle, \quad (7.1)$$

with a *unique* correspondence between eigenstates states n_a and n_b .

However, in many important cases our knowledge of quantum system's state is incomplete. This is especially unavoidable² when a relatively simple quantum system s of our interest (say, an electron or an atom) is in a contact with environment e – here understood in a most general sense, say, as all the whole Universe less system s – see Fig. 1. Then there is virtually no chance of making two or more experiments with exactly the same composite system, because it would imply a repeated preparation of the whole environment (including the experimenter :-)) in a certain quantum state - a rather challenging task, to put it mildly. In this case, it makes much more sense to consider a statistical ensemble of another kind, with *random* quantum states of the environment, though possibly with known macroscopic parameters (e.g., temperature, pressure, etc.).

In classical physics, such *mixed* ensembles are the subject of statistical (classical) mechanics.³ Let us see how they may be described in quantum mechanics. For the beginning, we need to assume

¹ For a broader discussion of statistical mechanics and physical kinetics, including those of quantum systems, the reader is referred to the SM part of this lecture note series.

² Most of the mixed ensemble analysis in this chapter will pertain also to the cases when the systems of interest are not in a contact with the environment currently, and our knowledge about them is incomplete by some other reason – for example, if they *had been* in such a contact at some time between their perfect preparation (in a certain quantum state) and the observation, or if such a perfect preparation is impossible (or impracticable, or undesirable :-)).

³ See, e.g., SM Sec. 2.1.

again that the coupling between the system of interest and its environment is weak in the sense accepted in the perturbation theory.⁴ In this case we can still use the bra- and ket-vectors of unperturbed states, that depend on different sets of variables (again, “belonging to different Hilbert spaces”). Then the most general quantum state of the whole Universe, still assumed to be pure,⁵ may be described as the following linear superposition:

$$|\alpha\rangle = \sum_{j,k} \alpha_{jk} |s_j\rangle \otimes |e_k\rangle. \quad (7.2)$$

Assumed
quantum
state of
Universe

The “only” difference between the description of such an *entangled* state and the superposition of separable states, described by Eq. (1), is that coefficients α_{jk} in the right-hand part of Eq. (2) are numbered with two indices: index j listing the quantum states of system s , and k numbering the (enormously large) set of quantum states of the environment. So, in a mixed ensemble a certain state s_j of the system of interest may coexist with different states of its environment.⁶ Of course, the enormity of the Hilbert space of the environment, i.e. the number of k -components in sum (2), strips us of any opportunity to make direct calculations using that sum. For example, according to the basic Eq. (4.125), in order to find the expectation value of an arbitrary observable A in state (2), we would need to calculate

$$\langle A \rangle = \langle \alpha | \hat{A} | \alpha \rangle = \sum_{\substack{j,j' \\ k,k'}} \alpha_{jk}^* \alpha_{j'k'} \langle e_k | \otimes \langle s_j | \hat{A} | s_{j'} \rangle \otimes | e_{k'} \rangle. \quad (7.3)$$

Even if we assume that $\{s\}$ and $\{e\}$ are sets of the basis states of, respectively, the system and the environment, and that each is full and orthonormal, Eq. (3) still includes a double sum over the enormous basis state set of the environment!

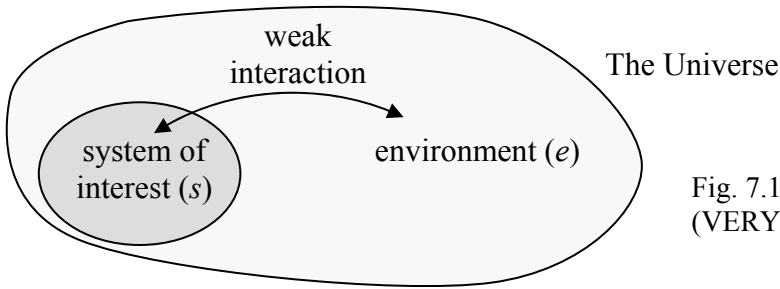


Fig. 7.1. Quantum system and its environment (VERY schematically :-).

However, let us consider a limited but the most important subset of operators – those of *intrinsic* observables, which depend only on the degrees of freedom of the system of interest (s). These operators commute do not act on environment’s degrees of freedom, and hence in Eq. (3) we may move the environment bra-vector $\langle e_k |$ over all the way to ket-vector $| e_{k'} \rangle$. Assuming, again, that the set of environmental eigenstates is full and orthonormal, Eq. (3) is now reduced to

⁴ In the opposite case, the very partition of the Universe into the system and the environment is impossible.

⁵ Whether this assumption is true is an interesting issue, still being debated (more by philosophers than by physicists), but it is widely believed that its solution is not critical for the validity of the results of this approach. In Sec. 6, I will offer a strong argument for this opinion - albeit not its strict proof.

⁶ Actually, such coexistence has been implied (but well hidden :-) in the derivation of the quantum-mechanical Golden Rule, which in all fairness, also belongs to the open systems class.

$$\langle A \rangle = \sum_{\substack{j,j' \\ k,k'}} \alpha_{jk}^* \alpha_{j'k'} \langle s_j | \hat{A} | s_{j'} \rangle \langle e_k | e_{k'} \rangle = \sum_{jj'} A_{jj'} \sum_k \alpha_{jk}^* \alpha_{j'k}. \quad (7.4)$$

This is already some relief, because we have “only” a single sum over k , but the main trick⁷ is still ahead. After the summation over k , the second sum in the last form of Eq. (4) is some function w of indices j and j' , so that, according to Eq. (4.96), this relation may be presented as

Expectation
value of
intrinsic
observable

$$\langle A \rangle = \sum_{jj'} A_{jj'} w_{j'j} = \text{Tr}(Aw), \quad (7.5)$$

where matrix w , with elements

Density
matrix:
definition

$$w_{jj'} \equiv \sum_k \alpha_{jk}^* \alpha_{j'k}, \quad \text{i.e. } w_{jj'} \equiv \sum_k \alpha_{jk} \alpha_{j'k}^*, \quad (7.6)$$

is called the *density matrix* of the system. Most importantly, Eq. (5) shows that the knowledge of this matrix allows the calculation of the expectation value of *any* intrinsic observable A (and, according to Eqs. (1.33)-(1.34), its r.m.s. fluctuation as well if necessary), even for the very general statistical ensemble of states (2). This is why let us have a very good look at the density matrix.

First of all, as we know very well by now that the expansion coefficients in superpositions of the type (2) may be always expressed as bra-kets; in our current case, we may write

$$\alpha_{jk} = \langle e_k | \otimes \langle s_j | \alpha \rangle. \quad (7.7)$$

Plugging this expression into Eq. (6), we get

$$w_{jj'} = \sum_k \alpha_{jk} \alpha_{j'k}^* = \langle s_j | \otimes \left(\sum_k \langle e_k | \alpha \rangle \langle \alpha | e_k \rangle \right) \otimes | s_{j'} \rangle = \langle s_j | \hat{w} | s_{j'} \rangle. \quad (7.8)$$

We see that from the point of our system (i.e. in its Hilbert space whose basis states may be numbered by indices j only), the density matrix is indeed just the matrix of some construct,⁸

Statistical
operator:
definition

$$\hat{w} \equiv \sum_k \langle e_k | \alpha \rangle \langle \alpha | e_k \rangle, \quad (7.9)$$

that is called the *statistical* (or “density”) *operator*. As evident from its definition (9), in contrast to the density matrix this operator does not depend on the choice of a particular basis s_j – just as all previous operators considered in this course, but in contrast to them, the statistical operator *does* depend on composite system’s state α , including the state of system s as well. However, in the j -space it is mathematically still an operator whose matrix elements obey all formulas of the bra-ket formalism.

In particular, due to its definition (6), the density operator is Hermitian:

$$w_{jj'}^* = \sum_k \alpha_{jk}^* \alpha_{j'k} = \sum_k \alpha_{j'k} \alpha_{jk}^* = w_{j'j}, \quad (7.10)$$

⁷ First suggested in 1927 by J. von Neumann.

⁸ Of course the “bra-kets” in this expression are not c -numbers, because state α is defined in a larger Hilbert space (of the environment plus the system of interest) than the basis states e_k (of the environment only).

so that according to the general analysis of Sec. 4.3, there should be a certain basis $\{w\}$ in which the matrix of this operator is diagonal:

$$w_{jj'}|_{\text{in } w} = w_j \delta_{jj'}. \quad (7.11)$$

Since any operator, in any basis may be presented in form (4.59), in basis $\{w\}$ we may write

$$\hat{w} = \sum_j |w_j\rangle w_j \langle w_j|. \quad (7.12)$$

Statistical
operator in
diagonalizing
basis

This expression reminds, but is not equivalent to Eq. (4.44) for the identity operator, that has been used so many times in this course, and in the basis w_j has the form

$$\hat{I} = \sum_j |w_j\rangle \langle w_j|. \quad (7.13)$$

In order to comprehend the meaning of coefficients w_j participating in Eq. (12), let us use Eq. (5) to calculate the expectation value of any observable A whose eigenstates coincide with those of the special basis set $\{w\}$:

$$\langle A \rangle = \text{Tr}(Aw) = \sum_{jj'} A_{jj'} w_j \delta_{jj'} = \sum_j A_j w_j. \quad (7.14)$$

Expectation
value of
 w_j -compatible
variable

where A_j is just the expectation value of observable A in state w_j . Hence, in order to comply with the general Eq. (1.37), real c -numbers w_j must have the physical sense of probabilities W_j of finding the system in state j . As the result, we can rewrite Eq. (12) in the form

$$\hat{w} = \sum_j |w_j\rangle W_j \langle w_j|. \quad (7.15)$$

In one ultimate case when only one of probabilities (say, $W_{j''}$) is different from zero,

$$W_j = \delta_{jj''}, \quad (7.16)$$

the system is evidently in a coherent (pure) state $w_{j''}$. Indeed, it is fully described by one ket-vector $|w_{j''}\rangle$, and we can use the general rule (4.86) to present it in another (arbitrary) basis $\{s\}$ as a coherent superposition

$$|w_{j''}\rangle = \sum_{j'} (U^\dagger)_{jj'} |s_{j'}\rangle = \sum_{j'} U_{jj'}^* |s_{j'}\rangle, \quad (7.17)$$

where U is the unitary matrix of transform from basis $\{w\}$ to basis $\{s\}$. According to Eqs. (11) and (16), in such a pure state the density matrix is diagonal in the $\{w\}$ basis,

$$w_{jj'}|_{\text{in } w} = \delta_{j,j''} \delta_{j',j''}, \quad (7.18a)$$

but not in an arbitrary basis. Indeed, using the general rule (4.92), we get

$$w_{jj'}|_{\text{in } s} = \sum_{l,l'} U_{jl}^\dagger w_{ll'}|_{\text{in } w} U_{l'j'} = U_{jj''}^\dagger U_{j''j'} = U_{j''j}^* U_{j''j'}. \quad (7.18b)$$

To make this result more transparent, let us denote matrix elements $U_{j''j} = \langle w_{j''}|s_j\rangle$ (that, for fixed j'' , depend on just one index j) by α_j ; then

Density
matrix
in a pure
state

$$w_{jj'}|_{\text{in } s} = \alpha_j^* \alpha_{j'}, \quad (7.19)$$

so that N^2 elements of the whole $N \times N$ matrix is determined by just *one* string of N c -numbers α_j . For example, for a two-level system ($N = 2$),

$$w|_{\text{in } s} = \begin{pmatrix} \alpha_1 \alpha_1^* & \alpha_2 \alpha_1^* \\ \alpha_1 \alpha_2^* & \alpha_2 \alpha_2^* \end{pmatrix}. \quad (7.20)$$

We see that the off-diagonal terms are, colloquially, “as large as the diagonal ones”, in the following sense:

$$w_{12} w_{21} = w_{11} w_{22}. \quad (7.21)$$

Since the diagonal terms have the sense of probabilities $W_{1,2}$ to find the system in the corresponding state, we may present Eq. (20) in the form

$$w = \begin{pmatrix} W_1 & (W_1 W_2)^{1/2} e^{i\varphi} \\ (W_1 W_2)^{1/2} e^{-i\varphi} & W_2 \end{pmatrix}. \quad (7.22)$$

The physical sense of the (real) constant φ is the phase shift between the coefficients in the linear superposition (17) that presents the pure state w_j in basis $s_{1,2}$.

Now let us consider a different statistical ensemble of two-level systems, that includes member states identical in all aspects (including similar probabilities $W_{1,2}$ in the same basis $s_{1,2}$), besides that the phase shifts φ are random, with the phase probability uniformly distributed over the trigonometric circle. Then the ensemble averaging is equivalent to averaging over φ from 0 to 2π , so that it kills the off-diagonal terms of the density matrix (22), and the matrix becomes diagonal. For a system with a time-independent Hamiltonian, such averaging is especially plausible in the basis of stationary states n of the system, in which phase φ is just the difference of integration constants in Eq. (4.158), and randomness is naturally produced by minor fluctuations of the energy difference $E_1 - E_2$. (In Sec. 3 we will study the dynamics of such *dephasing* process.) The mixed statistical ensemble of systems with the density matrix diagonal in the stationary state basis is called the *classical mixture*, and presents the limit opposite to the pure (coherent) state.

After that example, the reader should not be much shocked by the main claim⁹ of statistical mechanics that any large ensemble of similar systems in *thermodynamic* (or “thermal”) *equilibrium* is exactly such a classical mixture. Moreover, for systems in the thermal equilibrium with a much larger environment with fixed temperature T (such environment is usually called a *heat bath* or a *thermostat*) statistical physics gives¹⁰ a very simple expression, called the *Gibbs distribution*, for probabilities W_n :

$$W_n = \frac{1}{Z} \exp \left\{ -\frac{E_n}{k_B T} \right\}. \quad (7.23a)$$

Gibbs
distribution

⁹ This is essentially an alternative formulation of the basic postulate of statistical physics, called the *microcanonical distribution* - see, e.g., SM Sec. 2.2.

¹⁰ See, e.g., SM Sec. 2.4. The Boltzmann constant k_B is only needed if temperature is measured in non-energy units, say in kelvins.

where E_n is the eigenenergy of the corresponding stationary state, and Z is the normalization coefficient called the *statistical sum*

$$Z \equiv \sum_n \exp\left\{-\frac{E_n}{k_B T}\right\}. \quad (7.23b)$$

A detailed analysis of classical and quantum ensembles in thermodynamic equilibrium is the focus of statistical physics courses (such as my SM) rather than this course of quantum mechanics. However, I would still like to attract reader's attention to the key fact that, in contrast with the similarly-looking Boltzmann distribution for single particles,¹¹ the Gibbs distribution is absolutely general and is *not* limited to classical statistics. In particular, for quantum gases of indistinguishable particles, it is absolutely compatible with quantum statistics (such as the Bose-Einstein or Fermi-Dirac distributions) of the component particles. For example, if we use Eq. (23) to calculate the average energy of a 1D harmonic oscillator of frequency ω_0 in thermal equilibrium, we easily get¹²

$$W_n = \exp\left\{-n \frac{\hbar \omega_0}{k_B T}\right\} \left(1 - \exp\left\{-\frac{\hbar \omega_0}{k_B T}\right\}\right), \quad (7.24)$$

$$Z = \exp\left\{-\frac{\hbar \omega_0}{2k_B T}\right\} / \left(1 - \exp\left\{-\frac{\hbar \omega_0}{k_B T}\right\}\right), \quad (7.25)$$

$$\langle E \rangle = \sum_{n=0}^{\infty} W_n E_n = \frac{\hbar \omega_0}{2} \coth \frac{\hbar \omega_0}{2k_B T} = \frac{\hbar \omega_0}{2} + \frac{\hbar \omega_0}{\exp\{\hbar \omega_0 / k_B T\} - 1}. \quad (7.26a)$$

Harmonic
oscillator
in thermal
equilibrium

An alternative way to present the last result is to write

$$\langle E \rangle = \frac{\hbar \omega_0}{2} + \hbar \omega_0 \langle n \rangle, \quad \text{with } \langle n \rangle = \frac{1}{\exp\{\hbar \omega_0 / k_B T\} - 1}, \quad (7.26b)$$

and to interpret it as the fact that in addition to the so-called *zero-point energy* $\hbar \omega_0/2$ of the ground state, the oscillator (on the average) has $\langle n \rangle$ thermally-induced excitations, with energy $\hbar \omega_0$ each. In the harmonic oscillator, whose energy levels are equidistant, such a language is completely appropriate, because the transfer from any level to one just above it adds the same amount of energy, $\hbar \omega_0$, to the system. The above expression for $\langle n \rangle$ is actually the Bose-Einstein distribution (for the particular case of zero chemical potential);¹³ we see that it does not only contradict the Gibbs distribution (for the total energy of the system), but immediately follows from it.¹⁴

¹¹ See, e.g., SM Sec. 2.8.

¹² See, e.g., SM Sec. 2.5 - but mind a different energy reference level, $E_0 = \hbar \omega$, used in Eqs. (2.68)-(2.69), affecting the expression for Z . Actually, the calculation is so straightforward (just the summation of a geometric progression for the enumeration of Z) that it is highly recommended to the reader as a simple exercise.

¹³ See, e.g., SM Sec. 2.8.

¹⁴ Because of the fundamental importance of Eq. (26) for many fields of physics, let me remind the reader of its main properties. At low temperatures, $k_B T \ll \hbar \omega_0$, there are virtually no thermal excitations, $\langle n \rangle \rightarrow 0$, and the average energy of the oscillator is dominated by that of its ground state. In the opposite limit of high temperatures, $\langle n \rangle \rightarrow k_B T / \hbar \omega_0 \gg 1$, and $\langle E \rangle$ approaches the classical value $k_B T$ (following, for example, from the *equipartition theorem*, which assigns energy $k_B T/2$ to each quadratic contribution to system's energy – in the 1D oscillator case, to one potential and one kinetic energy term).

7.2. Coordinate representation and the Wigner function

For many applications of the density matrix to wave mechanics, its coordinate representation is convenient. (I will only discuss it for 1D case; the generalization to multi-dimension case is straightforward.) Following Eq. (4.47), it is natural to define the following function of two arguments (frequently also called the *density matrix*):

$$w(x, x') \equiv \langle x | \hat{w} | x' \rangle. \quad (7.27)$$

Inserting, into the right-hand part of this definition, two closure conditions (4.44) for an arbitrary (full and orthonormal) basis $\{s\}$, and then using Eq. (5.19), we get¹⁵

$$w(x, x') = \sum_{j, j'} \langle x | s_j \rangle \langle s_j | \hat{w} | s_{j'} \rangle \langle s_{j'} | x' \rangle = \sum_{j, j'} \psi_j(x) w_{jj'} |_{\text{in } s} \psi_{j'}^*(x'). \quad (7.28)$$

In the special basis $\{w\}$, in which the density matrix is diagonal, this expression is reduced to

$$w(x, x') = \sum_j \psi_j(x) W_j \psi_j^*(x'). \quad (7.29)$$

Let us discuss the properties of this function. At coinciding arguments, $x = x'$, this is just the probability density:¹⁶

$$w(x, x) = \sum_j \psi_j(x) W_j \psi_j^*(x) = \sum_j w_j(x) W_j = w(x). \quad (7.30)$$

However, the density matrix gives more information about the system than just the probability density. As the simplest example, let us consider a pure quantum state, with $W_j = \delta_{jj'}$, so that $\psi(x) = \psi_j(x)$, and

$$w(x, x') = \psi_j(x) \psi_j^*(x') = \psi(x) \psi^*(x'). \quad (7.31)$$

We see that the density matrix carries the information not only about the modulus but also the phase of the wavefunction. (Of course one may argue rather convincingly that in this ultimate limit the density-matrix description is redundant, because all this information is contained in the wavefunction itself.)

How may be the density matrix interpreted? In the simple case (31), we can write

$$|w(x, x')|^2 = w(x, x') w^*(x, x') = \psi(x) \psi^*(x) \psi(x') \psi^*(x') = w(x) w(x'), \quad (7.32)$$

so that the modulus squared of the density matrix may be just as the joint probability density to find the system at point x and point x' . For example, for a simple wave packet with the spatial extent δx , $w(x, x')$ is appreciable only if the both points are not farther than δx from the packet center, and hence from each other. The interpretation becomes more complex if we deal with an incoherent mixture of several wavefunctions, for example the classical mixture describing the thermodynamic equilibrium. In this case, we can use Eq. (23) to rewrite Eq. (29) as follows:

¹⁵ For now, I will focus on a fixed time instant (say, $t = 0$), and hence write $\psi(x)$ instead of $\Psi(x, t)$.

¹⁶ This fact is the historic origin of density matrix' name.

$$w(x, x') = \sum_n \psi_n(x) W_n \psi_n^*(x') = \frac{1}{Z} \sum_n \psi_n(x) \exp\left\{-\frac{E_n}{k_B T}\right\} \psi_n^*(x'). \quad (7.33)$$

As the simplest example, let us see what is the density matrix of a free (1D) particle in the thermal equilibrium. As we know very well, in this case, the set of energies $E_p = p^2/2m$ of stationary states (monochromatic waves) forms a continuum, so that we need to replace sum (33) by an integral, taking “delta-normalized” traveling wavefunctions (5.59) as eigenstates:

$$w(x, x') = \frac{1}{2\pi\hbar Z} \int_{-\infty}^{+\infty} \exp\left\{-\frac{ipx}{\hbar}\right\} \exp\left\{-\frac{p^2}{2mk_B T}\right\} \exp\left\{\frac{ipx'}{\hbar}\right\} dp. \quad (7.34)$$

This is a usual Gaussian integral, and may be worked out, as we have done repeatedly in Chapter 2 and beyond, by complementing the exponent to the full square of momentum plus a constant. The statistical sum Z may be also readily calculated,¹⁷

$$Z = (2\pi m k_B T)^{1/2}, \quad (7.35)$$

However, for what follows it is more useful to write the result for product wZ (the so-called *un-normalized density matrix*):

$$w(x, x')Z = \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{1/2} \exp\left\{-\frac{mk_B T(x-x')^2}{2\hbar^2}\right\}. \quad (7.36)$$

Free
particle
in thermal
equilibrium

This is a very interesting result: the density matrix depends only on the difference of its arguments, dropping to zero fast as the distance between points x and x' exceeds the following characteristic scale (called the *correlation length*)

$$x_c \equiv \left\langle (x-x')^2 \right\rangle^{1/2} = \frac{\hbar}{(mk_B T)^{1/2}}. \quad (7.37)$$

Free
particle's
correlation
length

This length may be interpreted in the following way. It is straightforward to use Eq. (23) to verify that the average energy $E_p = p^2/2m$ of a particle in the thermal equilibrium, i.e. in the classical mixture (33), equals $k_B T/2$ – this is just one more manifestation of the equipartition theorem. Hence the average momentum magnitude may be estimated as

$$p_c \equiv \langle p^2 \rangle^{1/2} = (2m\langle E \rangle)^{1/2} = (mk_B T)^{1/2}, \quad (7.38)$$

so that x_c is of the order of the minimal length allowed by the Heisenberg-like “uncertainty relation”:

$$x_c = \frac{\hbar}{p_c}. \quad (7.39)$$

¹⁷ Due to the delta-normalization of the eigenfunction, the density matrix for the free particle (and any system with continuous eigenvalue spectrum) is normalized as

$$\int_{-\infty}^{+\infty} w(x, x') Z dx' = \int_{-\infty}^{+\infty} w(x, x') Z dx = 1.$$

Notice that with the growth of temperature, the correlation length (37) goes to zero, and the density matrix (36) tends to the δ -function:

$$w(x, x')Z \Big|_{T \rightarrow \infty} \rightarrow \delta(x - x'). \quad (7.40)$$

Since in this limit the average kinetic energy of the particle is larger than its potential energy in *any* fixed potential profile, Eq. (40) is the general property of the density matrix (33).

Let us discuss the following curious feature of Eq. (36): if we replace $k_B T$ with $\hbar/i(t - t_0)$, and x' with x_0 , the un-normalized density matrix wZ for a free particle turns into the particle's propagator – see Eq. (2.49). This is not just an occasional coincidence. Indeed, in Chapter 2 we saw that the propagator of a system with an arbitrary stationary Hamiltonian may be expressed via the stationary eigenfunction as

$$G(x, t; x_0, t_0) = \sum_n \psi_n(x) \exp\left\{-i \frac{E_n}{\hbar}(t - t_0)\right\} \psi_n^*(x_0). \quad (7.41)$$

Comparing this expression with Eq. (33), we see that the replacements

$$\frac{i(t - t_0)}{\hbar} \rightarrow \frac{1}{k_B T}, \quad x_0 \rightarrow x', \quad (7.42)$$

turn the pure-state propagator G into the un-normalized density matrix wZ of the same system in thermodynamic equilibrium. This important fact, rooted in the formal similarity of the Gibbs distribution (23) with the Schrödinger equation's solution (1.67), enables a theoretical technique of the so-called *thermodynamic Green's functions*, which is especially productive in condensed matter physics.¹⁸

For our purposes, we can use Eq. (42) to recycle some of wave mechanics results, in particular the following formula for the harmonic oscillator's propagator

$$G(x, t; x_0, t_0) = \left(\frac{m\omega_0}{2\pi i \hbar \sin[\omega_0(t - t_0)]} \right)^{1/2} \exp\left\{ -\frac{m\omega_0[(x^2 + x_0^2)\cos[\omega_0(t - t_0)] - 2xx_0]}{2i\hbar \sin[\omega_0(t - t_0)]} \right\}. \quad (7.43)$$

that may be readily proved to satisfy the Schrödinger equation for Hamiltonian (5.95), with the appropriate initial condition, $G(x, t_0; x_0, t_0) = \delta(x - x_0)$. Making substitution (42), we immediately get

$$w(x, x')Z = \left(\frac{m\omega_0}{2\pi \hbar \sinh[\hbar\omega_0 / k_B T]} \right)^{1/2} \exp\left\{ -\frac{m\omega_0[(x^2 + x'^2)\cosh[\hbar\omega_0 / k_B T] - 2xx']}{2\hbar \sinh[\hbar\omega_0 / k_B T]} \right\}. \quad (7.44)$$

As a sanity check, at very low temperatures, $k_B T \ll \hbar\omega_0$, both hyperbolic functions, participating in this expression, are very large and nearly equal, and Eq. (44) yields

$$w(x, x')Z \Big|_{T \rightarrow 0} \rightarrow \left[\left(\frac{m\omega_0}{\pi \hbar} \right)^{1/4} \exp\left\{ -\frac{m\omega_0 x^2}{\hbar} \right\} \right] \times \exp\left\{ -\frac{\hbar\omega_0}{2k_B T} \right\} \times \left[\left(\frac{m\omega_0}{\pi \hbar} \right)^{1/4} \exp\left\{ -\frac{m\omega_0 x'^2}{\hbar} \right\} \right]. \quad (7.45)$$

¹⁸ I will have no time to discuss this technique, and have to refer the interested reader to special literature. Probably, the most famous text of that field is A. Abrikosov, L. Gor'kov, and I. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, 1963. (Later reprintings are available from Dover.)

In each of the square brackets we can readily recognize the ground state's wavefunction (2.269), while the middle exponent is just the statistical sum (24) in the low-temperature limit when it is dominated by the ground-level contribution:

$$Z|_{T \rightarrow 0} \rightarrow \exp\left\{-\frac{\hbar\omega_0}{2k_B T}\right\}. \quad (7.46)$$

As a result, Z in both parts of Eq. (45) may be cancelled, and the density matrix in this limit is described by Eq. (31), with the ground state as the only state of the system. This is natural when temperature is too low for the excitation of any other state.

Returning to arbitrary temperatures, Eq. (44) in coinciding arguments gives the following expression for the probability density:¹⁹

$$w(x, x)Z = w(x)Z = \left(\frac{m\omega_0}{2\pi\hbar \sinh[\hbar\omega_0 / k_B T]}\right)^{1/2} \exp\left\{-\frac{m\omega_0 x^2}{\hbar} \tanh \frac{\hbar\omega_0}{2k_B T}\right\}. \quad (7.47)$$

This is just a Gaussian function of x , with the following variance:

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega_0} \coth \frac{\hbar\omega_0}{2k_B T}. \quad (7.48)$$

In order to compare this result with our earlier ones, it is useful to recast it as

$$\langle U \rangle = \frac{m\omega_0^2}{2} \langle x^2 \rangle = \frac{\hbar\omega_0}{4} \coth \frac{\hbar\omega_0}{2k_B T}. \quad (7.49)$$

Comparing this expression with Eq. (26), we see that the average value of potential energy is exactly one half of the total energy - the other half being the average kinetic energy. This is what we could expect, because according to Eqs. (5.129)-(5.130), such relation holds for each Fock state and hence should also hold for their classical mixture.

Unfortunately, besides the trivial case (30) of coinciding arguments, it is hard to give a straightforward interpretation of the density function in terms of system measurements. This is a fundamental difficulty that has been well explored in terms of the *Wigner function* (sometimes called the “Wigner-Ville distribution”)²⁰ defined as

$$W(X, P) \equiv \frac{1}{2\pi\hbar} \int w\left(X + \frac{\tilde{X}}{2}, X - \frac{\tilde{X}}{2}\right) \exp\left\{-\frac{iP\tilde{X}}{\hbar}\right\} d\tilde{X}. \quad (7.50)$$

Wigner
function:
definition

¹⁹ I have to confess that this notation is imperfect, because from the point of view of rigorous mathematics, $w(x, x')$ and $w(x)$ are different functions, and so are $w(p, p')$ and $w(p)$ used below. In the perfect world, I would use different letters for them all, but I desperately want to stay with “ w ” for all the probability densities, and there are not so many good different fonts for this letter. Let me hope that the difference between these functions is clear from their arguments, and from the context.

²⁰ It was introduced in 1932 by E. Wigner on the basis of a general (*Weyl-Wigner*) transform suggested by H. Weyl in 1927, and re-derived in 1948 by J. Ville on a different mathematical basis.

From the mathematical standpoint, this is just the Fourier expansion of the density matrix in one of two new coordinates (Fig. 2) defined by relations

$$x = X + \frac{\tilde{X}}{2}, \quad x' = X - \frac{\tilde{X}}{2}. \quad (7.51)$$

Physically, the new argument $X = (x + x')/2$ may be understood as the average position of the particle during the time interval $(t - t')$, while $\tilde{X} = x - x'$ as the distance passed by the particle during that time interval, so that P may be interpreted as the characteristic momentum of a particle during that motion. As a result, the Wigner function is a construct intended to characterize the system spread simultaneously in the coordinate and momentum space - for 1D systems, on the phase plane $[X, P]$ that we considered before – see Fig. 5.6. Let us see how fruitful these intentions are.

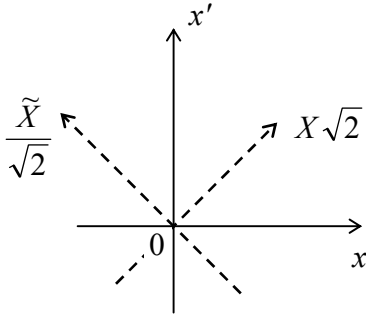


Fig. 7.2. Coordinates X and $\tilde{X}$ employed in the Weyl-Wigner transform (50). They differ from the coordinates obtained by the rotation of the reference frame by angle $\pi/2$ only by coefficients $\sqrt{2}$, describing scale stretching.

First of all, we may write the Fourier transform reciprocal to Eq. (50):

$$w\left(X + \frac{\tilde{X}}{2}, X - \frac{\tilde{X}}{2}\right) = \int W(X, P) \exp\left\{+ \frac{iP\tilde{X}}{\hbar}\right\} dP. \quad (7.52)$$

For the particular case $\tilde{X} = 0$, this relation yields

$$w(X) \equiv w(X, X) = \int W(X, P) dP. \quad (7.53)$$

Hence the integral of the Wigner function over momentum P gives the probability density to find the system at point X .

Actually, the function has the same property for integration over X . To prove that, we should first introduce the momentum representation of the density matrix, in the full analogy with its coordinate representation (27):

$$w(p, p') \equiv \langle p | \hat{w} | p' \rangle. \quad (7.54)$$

Inserting, as usual, two identity operators, in the form given by Eq. (5.21), into the right hand part of this equality, we can get the following relation between the momentum and coordinate representations:

$$w(p, p') \equiv \langle p | \hat{w} | p' \rangle = \iint dx dx' \langle p | x \rangle \langle x | \hat{w} | x' \rangle \langle x' | p' \rangle = \frac{1}{2\pi\hbar} \iint dx dx' \exp\left\{-\frac{ipx}{\hbar}\right\} w(x, x') \exp\left\{\frac{ip'x'}{\hbar}\right\}. \quad (7.55)$$

This is of course nothing else than the unitary transform of an operator from the x -basis to p -basis, and is similar to the first form of Eq. (5.67).²¹ For coinciding arguments, $p = p'$, Eq. (55) is reduced to

$$w(p) \equiv w(p, p) = \frac{1}{2\pi\hbar} \iint dx dx' w(x, x') \exp\left\{-\frac{ip(x-x')}{\hbar}\right\}. \quad (7.56)$$

Using Eq. (29) and then Eq. (5.60), this function may be presented as

$$w(p) = \frac{1}{2\pi\hbar} \sum_j W_j \iint dx dx' \psi_j(x) \psi_j^*(x) \exp\left\{-\frac{ip(x-x')}{\hbar}\right\} = \sum_j W_j \varphi_j(p) \varphi_j^*(p), \quad (7.57)$$

and hence interpreted as the probability density of the particle's momentum at point p . Now, in variables (51), Eq. (56) has the form

$$w(p) = \frac{1}{2\pi\hbar} \iint w\left(X + \frac{\tilde{X}}{2}, X - \frac{\tilde{X}}{2}\right) \exp\left\{-\frac{iP\tilde{X}}{\hbar}\right\} d\tilde{X} dX. \quad (7.58)$$

Comparing this equality with definition (50) of the Wigner function, we see that

$$w(P) = \int W(X, P) dX. \quad (7.59)$$

Thus, according to Eqs. (53) and (59), the integrals of the Wigner function over either the coordinate or momentum give the probability densities to find them at certain values of these variables. This is of course the main requirement to any candidate joint probability density, $\rho(X, P)$, to find a classical representation point of a stochastic system on the phase plane $[X, P]$.²²

Let us look how does the Wigner function look for the simplest systems in the thermodynamic equilibrium. For a free 1D particle, we can use Eq. (34), ignoring for simplicity the normalization issues:

$$W(X, P) \propto \int_{-\infty}^{+\infty} \exp\left\{-\frac{mk_B T \tilde{X}^2}{2\hbar^2}\right\} \exp\left\{-\frac{iP\tilde{X}}{\hbar}\right\} d\tilde{X}. \quad (7.60)$$

The usual Gaussian integration yields:

$$W(X, P) = \text{const} \times \exp\left\{-\frac{P^2}{2mk_B T}\right\}. \quad (7.61)$$

Thermal
equilibrium:
free
particle

We see that the function is independent of X (as it should be for this translational-invariant system), and coincides with the Gibbs distribution (23). We could get the same result directly from classical statistics. This is natural, because as we know from Sec. 2.2, the free motion is essentially not quantized – at least in terms of its energy and momentum.

Now let us consider a substantially quantum system, the harmonic oscillator. Plugging Eq. (44) into Eq. (50), for that system in thermal equilibrium it is easy to show (and hence is left for reader's exercise) that the Wigner function is also Gaussian, but now in both its arguments:

²¹ Note that the last line of Eq. (5.67) is invalid for the density operator $\hat{w}$, because it is *not* local!

²² Such density, which would express the probability dW to find the system in a small area of the phase plane as $dW = \rho(X, P) dX dP$, is the basic notion of (1D) classical statistics – see, e.g., SM Sec. 2.1.

$$W(X, P) = \text{const} \times \exp \left\{ -C \left[\frac{m\omega_0^2 X^2}{2} + \frac{P^2}{2m} \right] \right\}, \quad (7.62)$$

though coefficient C is now different from $1/k_B T$, and tends to that limit only at high temperatures, $k_B T \gg \hbar\omega_0$. Moreover, for the Glauber state it also gives a very plausible result – a Gaussian distribution similar to Eq. (62), but shifted to the central point of the state – see Sec. 5.5.²³

Unfortunately, for some other possible states of the harmonic oscillator, e.g., any pure Fock state with $n > 0$, the Wigner function takes negative values in some regions of the $[X, P]$ plane - Fig. 3.²⁴

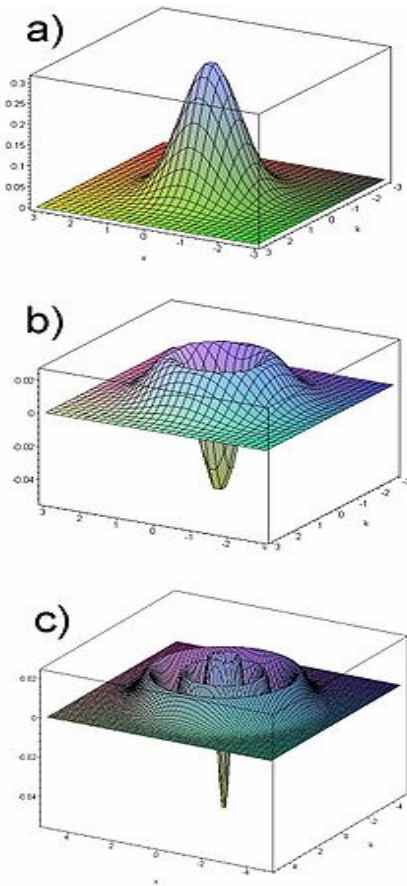


Fig. 7.3. The Wigner function of several Fock states of a harmonic oscillator: (a) $n = 0$, (b) $n = 1$; (c) $n = 5$. Adapted from http://en.wikipedia.org/wiki/Wigner_function.

The same is true for most other quantum systems. Indeed, this fact could be predicted just by looking at definition (50) applied to a pure quantum state, in which the density function may be factored – see Eq. (31):

²³ Please note that in notations of that section, arguments $\{X, P\}$ of the Wigner function should be replaced with $\{x, p\}$, and capital letters saved for the Cartesian coordinates of the central point (5.133), i.e. the classical complex amplitude of the oscillations.

²⁴ Spectacular experimental measurements of this function (for $n = 0$ and $n = 1$) were carried out recently by E. Bimbard *et al.*, *Phys. Rev. Lett.* **112**, 033601 (2014).

$$W(X, P) = \frac{1}{2\pi\hbar} \int \psi\left(X + \frac{\tilde{X}}{2}\right) \psi^*\left(X - \frac{\tilde{X}}{2}\right) \exp\left\{-\frac{iP\tilde{X}}{\hbar}\right\} d\tilde{X}. \quad (7.63)$$

Wigner
function:
1D pure
quantum
state

Changing argument P (say, at fixed X), we are essentially changing the spatial “frequency” (wavenumber) of the wavefunction product’s Fourier component we are calculating, and we know that Fourier images typically change sign as the frequency is changed. Hence the wavefunctions should have some high-symmetry properties to avoid this effect. Indeed, the Gaussian functions (describing, for example, the Glauber states, and as the particular case, the ground state of the harmonic oscillator) have such a symmetry, but many other functions do not.

Hence the Wigner function cannot be used in the role of classical probability density $\rho(X, P)$, otherwise we would get a negative probability for measurement in certain intervals $dXdP$ – the notion hard to interpret. However, the Wigner function is still used for a semi-quantitative interpretation of states of open quantum systems.

7.3. Open system dynamics: Dephasing

So far we have discussed the density matrix as something given. Now let us discuss the evolution of the matrix in time, starting from the simplest case when the system is in state (15) with *time-independent* probabilities W_j . In the Schrödinger picture we can rewrite Eq. (15) as

$$\hat{w}(t) = \sum_j |w_j(t)\rangle W_j \langle w_j(t)|. \quad (7.64)$$

Differentiating this equation by parts, and using Eqs. (4.157)-(4.158), with the account of the Hermitian nature of the Hamiltonian operator, we get

$$\begin{aligned} i\hbar\dot{\hat{w}} &= i\hbar \sum_j \left[\dot{w}_j(t) \rangle W_j \langle w_j(t) | + | w_j(t) \rangle W_j \langle \dot{w}_j(t) | \right] = \sum_j \left[\hat{H} | w_j(t) \rangle W_j \langle w_j(t) | - | w_j(t) \rangle W_j \langle w_j(t) | \hat{H} \right] \\ &= \hat{H} \sum_j | w_j(t) \rangle W_j \langle w_j(t) | - \sum_j | w_j(t) \rangle W_j \langle w_j(t) | \hat{H}. \end{aligned} \quad (7.65)$$

Now using Eq. (64) again (twice), we get the so-called *von Neumann equation*²⁵

$$i\hbar\dot{\hat{w}} = [\hat{H}, \hat{w}]. \quad (7.66)$$

von Neumann
equation

This equation is similar in structure to Eq. (4.199) describing the time evolution of the Heisenberg-picture operators:

$$i\hbar\dot{\hat{A}} = [\hat{A}, \hat{H}], \quad (7.67)$$

besides the operator order in the commutator, i.e., the sign of the right-hand part. This is quite natural, because Eq. (66) belongs to the Schrödinger picture, while Eq. (67) to the Heisenberg picture of the quantum dynamics.

²⁵ In many texts, it is called the “Liouville equation”, due to the philosophical proximity to the classical Liouville theorem for the distribution function $\rho(X, P)$ or its multi-dimensional analog – see, e.g., SM Sec. 6.1, in particular Eq. (6.5).

In the general case when a system, initially out of equilibrium, comes into a contact with the environment, probabilities W_j change, and dynamics is described by equations more complex than Eq. (66). However, we still can use this equation to discuss, using a simple model, the second (after the energy relaxation) major effect of the environment, *dephasing* (also called “decoherence”).²⁶ Let us consider the following model of a system interacting (weakly!) with environment:²⁷

System's
interaction
with
environment

$$\hat{H} = \hat{H}_s + \hat{H}_e\{\lambda\} + \hat{H}_{\text{int}}. \quad (7.68)$$

Let us consider the simplest, two-level system, taking its Hamiltonian in the simplest form,

$$\hat{H}_s = a_z \hat{\sigma}_z, \quad (7.69)$$

(as we know from Sec. 4.6, such Hamiltonian is sufficient to avoid the energy level degeneracy), and a factorable (bilinear) interaction - cf. Eq. (6.148) and its discussion:

$$\hat{H}_{\text{int}} = -\hat{f}\{\lambda\} \hat{\sigma}_z. \quad (7.70)$$

Here $\hat{f}$ is a Hermitian operator depending only on the set $\{\lambda\}$ of environmental degrees of freedom (“coordinates”). These coordinates belong to the Hilbert space different from that of the two-level system, and hence operators $\hat{f}\{\lambda\}$ and $\hat{H}_e\{\lambda\}$ (that describes the environment) commute with $\hat{\sigma}_z$ - and any other intrinsic operator of the two-level system. Of course, any realistic $\hat{H}_e\{\lambda\}$ is very complex, so that it may be surprising how much we will be able to achieve without specifying it.

Before we proceed to solution, let me remind the reader of the important two-level systems that may be described by this model. The first example is an electron in an external magnetic field of a fixed direction (taken for axis z), which includes both an average component $\langle \mathcal{B}_z \rangle$ and a random (fluctuating) component $\tilde{\mathcal{B}}_z$. As it follows from the discussion in Chapter 4, it may be described by Hamiltonian (68)-(70) with

$$a_z = \mu_B \langle \mathcal{B}_z \rangle, \quad -\hat{f} = \mu_B \tilde{\mathcal{B}}_z. \quad (7.71)$$

The second important example is a particle in a double-quantum-well potential (Fig. 4), with a barrier between them sufficiently high to be impenetrable, and an additional force $F(t)$ exerted by the environment. If the force is sufficiently weak, we can neglect its effects on the shape of quantum wells and hence on the localized wavefunctions $\psi_{L,R}$, so that the force effect is reduced to the variation of the difference $E_L - E_R = F(t)\Delta x$ between well eigenenergies. As a result, it may be described by Eqs. (608)-(70) with

$$a_z \approx \langle F \rangle \Delta x / 2; \quad -\hat{f} \approx \tilde{F} \Delta x / 2. \quad (7.72)$$

²⁶ Another example when W_j are constant in time, and hence Eq. (66) is valid, is the thermodynamic equilibrium. However, in this case the statistical operator is diagonal in the stationary state basis and hence commutes with the Hamiltonian. Hence the right-hand part of Eq. (66) vanishes, and it shows that the density matrix does not evolve in time at all – as it should.

²⁷ Though this model works very well in many cases (see the examples given below), it is not adequate for a particle interacting with the environment of *similar* particles. In this case the methods discussed in the next chapter are more relevant.

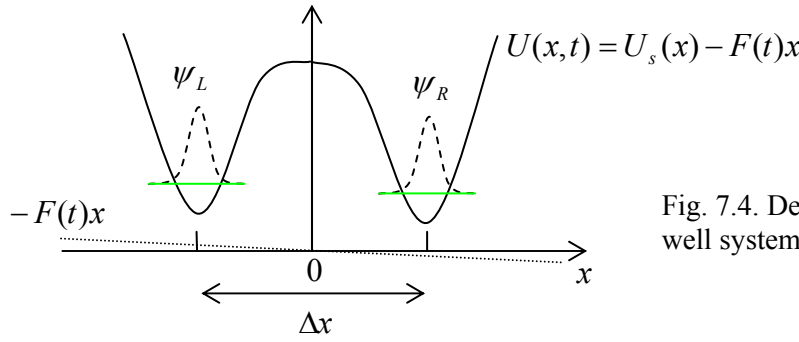


Fig. 7.4. Dephasing in a double quantum well system.

Returning to the general model (68)-(70), let us start its analysis from writing the usual equation of motion for the Heisenberg operator $\hat{\sigma}_z$:²⁸

$$i\hbar \dot{\hat{\sigma}}_z = [\hat{\sigma}_z, \hat{H}] = (a_z - \hat{f})[\hat{\sigma}_z, \hat{\sigma}_z] = 0, \quad (7.73)$$

so that operator $\hat{\sigma}_z$ does not evolve in time. What does this mean for the observables? For an arbitrary density matrix of the two-level system,

$$w = \begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix}, \quad (7.74)$$

we can readily calculate the trace of operator $\hat{\sigma}_z$ (since operator traces are basis – independent, we can do this in any basis, in particular in the usual z -basis):

$$\text{Tr}(\hat{\sigma}_z \hat{w}) = \text{Tr}(\sigma_z w) = \text{Tr} \left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix} \right] = w_{11} - w_{22} = W_1 - W_2. \quad (7.75)$$

Hence, according to Eq. (5), $\hat{\sigma}_z$ may be considered the operator for observable $W_1 - W_2$, so that in the case (73), the difference $W_1 - W_2$ does not depend on time, and since the sum of the probabilities is also fixed, $W_1 + W_2 = 1$, both of them are constant. (The physics of this result is especially clear for the model shown in Fig. 4: since the potential barrier separating the quantum wells is so high that tunneling through it is negligible, the interaction with environment cannot move the system from well into another one. It may look like nothing interesting may happen in such situation, but in a minute we will see this is not true.) Hence, we may use the von Neumann equation (66) for the density matrix evolution (in the Schrödinger picture). In the usual z -basis:

$$\begin{aligned} i\hbar \dot{w} &\equiv i\hbar \begin{pmatrix} \dot{w}_{11} & \dot{w}_{12} \\ \dot{w}_{21} & \dot{w}_{22} \end{pmatrix} = [H, w] = (a_z - \hat{f})[\sigma_z, w] \\ &= (a_z - \hat{f}) \left\{ \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix} - \begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\} = (a_z - \hat{f}) \begin{pmatrix} 0 & 2w_{12} \\ -2w_{21} & 0 \end{pmatrix}. \end{aligned} \quad (7.76)$$

²⁸ This can be done because we may consider the whole system, including the environment, as a Hamiltonian one – see Eq. (68).

This means that though the diagonal elements, i.e., the probabilities of the states, do not evolve in time (as we already know), the off-diagonal coefficients do change; for example,

$$i\hbar\dot{w}_{12} = 2(a_z - \hat{f})w_{12}, \quad (7.77)$$

with a similar but complex-conjugate equation for w_{21} . The solution of the linear differential equation (77) is straightforward, and yields

$$w_{12}(t) = w_{12}(0) \exp\left\{-i\frac{2a_z}{\hbar}t\right\} \exp\left\{i\frac{2}{\hbar}\int_0^t \hat{f}(t')dt'\right\}. \quad (7.78)$$

The first exponent is a deterministic c -number factor, while in the second one $\hat{f}(t) \equiv \hat{f}\{\lambda(t)\}$ is still an operator in the Hilbert space of the environment, and, from the point of view of the system of our interest, a random function of time.

Let us start from the limit when the environment behaves classically.²⁹ In this case, the operator in Eq. (78) may be considered as a *classical* random function of time $f(t)$, provided that we average the result over the ensemble of many functions $f(t)$ describing many (macroscopically similar) experiments. For a small time interval $t = dt \rightarrow 0$, we can use the Taylor expansion of the exponent, truncating it after the quadratic term:

$$\begin{aligned} \left\langle \exp\left\{i\frac{2}{\hbar}\int_0^{dt} f(t')dt'\right\} \right\rangle &\approx 1 + \left\langle i\frac{2}{\hbar}\int_0^{dt} f(t')dt' \right\rangle + \left\langle \frac{1}{2}\left(i\frac{2}{\hbar}\int_0^{dt} f(t')dt'\right)\left(i\frac{2}{\hbar}\int_0^{dt} f(t'')dt''\right) \right\rangle \\ &= 1 + i\frac{2}{\hbar}\int_0^{dt} \langle f(t') \rangle dt' - \frac{2}{\hbar^2}\int_0^{dt} dt' \int_0^{dt} dt'' \langle f(t')f(t'') \rangle = 1 - \frac{2}{\hbar^2}\int_0^{dt} dt' \int_0^{dt} dt'' K_f(t' - t''). \end{aligned} \quad (7.79)$$

Here we have used the fact that the first average is equal to zero (it is evident from Eqs. (69)-(70) that if f had any average component, it could be included into parameter a), while the second average, called the *correlation function*, in a statistically- (i.e. macroscopically-) stationary state of environment may only depend on the time difference $\tau \equiv t' - t''$:

$$\langle f(t')f(t'') \rangle \equiv K_f(t' - t'') = K_f(\tau). \quad (7.80)$$

If this difference is much larger than some time scale τ_c , called the *correlation time* of the random force, the values $f(t')$ and $f(t'')$ are completely independent (*uncorrelated*), as illustrated in Fig. 5a, so that the correlation function has to tend to zero. On the other hand, at $\tau = 0$, i.e. $t' = t''$, the correlation function is just the variance of f :

$$K_f(0) = \langle f^2 \rangle, \quad (7.81)$$

and has to be positive. As a result, the function looks (qualitatively) like the sketch in Fig. 5b.

²⁹ This assumption is not in any contradiction with the quantum treatment of the two-level system, because a typical environment has very dense energy spectrum, so that the distances between them may be readily bridged by thermal excitations of energies $\sim k_B T \ll 2a_z$, often making its essentially classical.

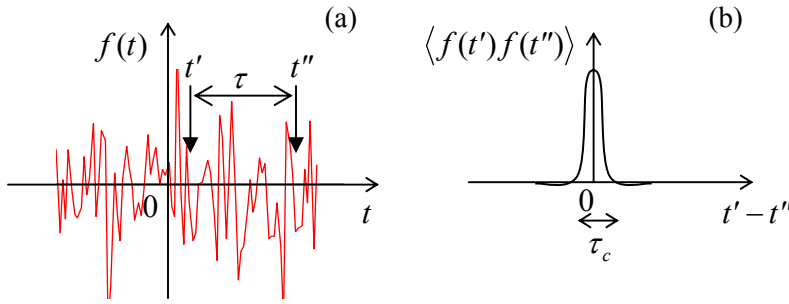


Fig. 7.5. (a) Typical random process and (b) its correlation function – schematically.

Hence, if we are only interested in time differences τ much longer than τ_c , we may approximate $K_f(\tau)$ with a delta-function. Let us take it in the following convenient form

$$K_f(\tau) \approx \hbar^2 D_\phi \delta(\tau), \quad (7.82)$$

Phase
diffusion
coefficient

where D_ϕ is a positive constant called the *phase diffusion coefficient*. The origin of this term stems from the very similar effect of diffusion of atoms or small solid particles in real space – the so-called (the *Brownian motion*).³⁰ Indeed, if a small classical particle moves in a highly viscous medium, its velocity is approximately proportional to the external force. Hence, if the random hits of a 1D particle by the molecules may be described by a force which obeys a law similar to Eq. (82), the velocity (along any Cartesian coordinate) is also *delta-correlated*:

$$\langle v(t) \rangle = 0, \quad \langle v(t')v(t'') \rangle = 2D\delta(t' - t''). \quad (7.83)$$

Now we can integrate the kinematic equation $\dot{x} = v$, to calculate particle's deviation from the initial position,

$$x(t) - x(0) = \int_0^t v(t') dt', \quad (7.84)$$

and its the variance:

$$\langle (x(t) - x(0))^2 \rangle = \left\langle \int_0^t v(t') dt' \int_0^t v(t'') dt'' \right\rangle = \int_0^t dt' \int_0^t dt'' \langle v(t')v(t'') \rangle = \int_0^t dt' \int_0^t dt'' 2D\delta(t' - t'') = 2Dt. \quad (7.85)$$

This is the famous law of diffusion, showing that the r.m.s. deviation of the particle from the initial point grows with time as $(2Dt)^{1/2}$, where constant D is called the *diffusion coefficient*.

Returning to the diffusion of the quantum-mechanical phase, using Eq. (82), the last double integral in Eq. (79) yields $\hbar^2 D_\phi dt$, so that

$$\langle w_{12}(dt) \rangle = w_{12}(0) \exp \left\{ -i \frac{2a_z}{\hbar} dt \right\} (1 - 2D_\phi dt). \quad (7.86)$$

Applying this formula to sequential time intervals,

³⁰ The theory of this phenomenon, first observed experimentally by biologist R. Brown in the early 1800s, was pioneered by A. Einstein in 1905 (see in particular Eq. (206) below) and developed in detail by M. Smoluchowski in 1906-1907, and A. Fokker in 1913.

$$\langle w_{12}(2dt) \rangle = \langle w_{12}(dt) \rangle \exp\left\{-i\frac{2a_z}{\hbar}dt\right\} (1 - 2D_\varphi dt) = w_{12}(0) \exp\left\{-i\frac{2a_z}{\hbar}2dt\right\} (1 - 2D_\varphi dt)^2, \quad (7.87)$$

etc., for a finite time $t = Ndt$, in the limit $N \rightarrow \infty$ and $dt \rightarrow 0$ (at fixed t) we get,³¹

$$\langle w_{12}(t) \rangle = w_{12}(0) \exp\left\{-i\frac{2a_z}{\hbar}t\right\} \lim_{N \rightarrow \infty} \left(1 - 2D_\varphi \frac{1}{N}\right)^N. \quad (7.88a)$$

By the definition of the natural logarithm base e ,³² this limit is just $\exp\{-2D_\varphi t\}$, so that, finally:

Two-level
system's
dephasing

$$\langle w_{12}(t) \rangle = w_{12}(0) \exp\left\{-i\frac{2a_z}{\hbar}t\right\} \exp\{-2D_\varphi t\} \equiv w_{12}(0) \exp\left\{-i\frac{2a_z}{\hbar}t\right\} \exp\left\{-\frac{t}{T_2}\right\}. \quad (7.88b)$$

So, due to coupling to environment, the off-diagonal elements of the density matrix decay with the characteristic *dephasing time* $T_2 = 1/2D_\varphi$, providing a natural evolution from the density matrix (22) of a pure state, to the diagonal matrix,

$$w = \begin{pmatrix} W_1 & 0 \\ 0 & W_2 \end{pmatrix}, \quad (7.89)$$

with the same probabilities $W_{1,2}$, describing a fully dephased (incoherent) classical mixture.

Our simple model offers a very clear look at the nature of decoherence: “force” $f(t)$, exerted by the environment, “shakes” the energy difference between two eigenstates of the system and hence the instant velocities $2(a_z - f)/\hbar$ of their mutual phase shift $\varphi(t)$ – cf. Eq. (24). Due to randomness of the force, $\varphi(t)$ performs a random walk around the trigonometric circle, so that eventually, averaging of its trigonometric functions $\exp\{\pm i\varphi\}$ over the possible states of environment yields zero, killing the off-diagonal elements of the density matrix. Our analysis, however, has left open two important issues:

- (i) Is it approach valid for a quantum description of a typical environment?
- (ii) If yes, what is D_φ ?

7.4. Fluctuation-dissipation theorem

Similar questions may be asked about a more general situation, when the Hamiltonian $\hat{H}_s$ of the system of interest (s), in the composite Hamiltonian (68), is not specified at all, but the interaction between that system its environment still has the bilinear form similar to Eqs. (70) and (6.130):

$$\hat{H}_{\text{int}} = -\hat{F}\{\lambda\} \hat{x}, \quad (7.90)$$

³¹ This result is valid only if approximation (82) may be applied at time interval dt which, in turn, should be much smaller than T_2 , i.e. if the dephasing time is much longer than the environment's correlation time τ_c . This requirement is usually well satisfied, because in most environments, τ_c very short. For example, in the original Brownian motion experiments with few- μm ink particles in water, it is of the order of the average interval between sequential molecular impacts, of the order of 10^{-21} s.

³² See, e.g., MA Eq. (1.2a).

where x is some observable of the subsystem s (say, a generalized coordinate or a generalized momentum). It may look incredible that in this very general situation one may make a very simple and powerful statement about the statistical properties of the generalized external force F , under only two (interrelated) conditions – which are satisfied in a huge number of cases of interest:

(i) the coupling of system s of interest to environment e is weak - in the sense of the perturbation theory (see Chapter 6), and

(ii) the environment may be considered as staying in thermodynamic equilibrium, with certain temperature T , regardless of the process in the system of interest.³³

This famous statement is called the *fluctuation-dissipation theorem* (FDT).³⁴ Due to the importance of this fundamental result, let me derive it.³⁵

Since by writing Eq. (68) we treat the whole system ($s + e$) as a Hamiltonian one,³⁶ we may use the Heisenberg equation (4.199) to write

$$i\hbar\dot{\hat{F}} = [\hat{F}, \hat{H}] = [\hat{F}, \hat{H}_e], \quad (7.91)$$

because, as was discussed in the last section, operator $\hat{F}\{\lambda\}$ commutes with operators $\hat{H}_s$ and $\hat{x}$. Generally, very little may be done with this equation, because the time evolution of the environment's Hamiltonian depends, in turn, on that of the force. This is where the perturbation theory becomes indispensable. Let us decompose the external force's operator into the following sum:

$$\hat{F}\{\lambda\} = \langle \hat{F} \rangle + \hat{\tilde{F}}(t), \quad \text{with } \langle \hat{\tilde{F}}(t) \rangle = 0, \quad (7.92)$$

where (until further notice) sign $\langle \dots \rangle$ means the statistical averaging over the environment alone.³⁷ From the point of view of system s , the first term of the sum (still an operator!) describes the average response

³³ The most frequent example of violation of these conditions is environment's overheating by the energy flow from the subsystem. I leave it to the reader to estimate the overheating of a standard physical laboratory room by a typical dissipative quantum process – the emission of an optical photon by an atom. (*Hint*: extremely small.)

³⁴ The FDT was first derived by H. Callen and T. Welton in 1951, on the background of an earlier derivation of its classical limit by H. Nyquist in 1928, and the pioneering 1905 work by A. Einstein – see below.

³⁵ The FDT may be proved in several ways which are different from, and shorter than the one given in this section – see, e.g., either SM Secs. 5.5 and 5.6 (based on H. Nyquist's arguments), or the original paper by H. Callen and T. Welton, *Phys. Rev.* **83**, 34 (1951) - wonderful in its clarity. The longer approach I describe here, besides giving the important *Kubo formula* (109) as a byproduct, is a very useful exercise in the operator manipulation and the perturbation theory in its integral form, different from the differential form used in Chapter 6. If the reader is not interested in this exercise, he or she may skip the derivation and jump directly to the result expressed by Eq. (134), which uses the notions defined by Eqs. (114) and (123).

³⁶ We can always do that if the local environment is large enough, so that the processes in our subsystem would not depend on the type of boundary between it and the external environment; in particular we may assume the total system closed, i.e. Hamiltonian.

³⁷ For usual (“ergodic”) environments, without intrinsic long-term memories, this statistical averaging over an ensemble of environments is equivalent to averaging over relatively short times - much longer than the correlation time τ_c of the environment, but still much shorter than the characteristic time of evolution of the system under analysis, such as the dephasing time T_2 and the energy relaxation time T_1 – both still to be calculated. As was already mentioned, in most practical environments, τ_c is very short. Thus, for relatively “massive” (inertial) systems of interest the separation of the averaging into two steps is well justified.

of the environment to the system dynamics (possibly, including such irreversible effects as friction/viscosity), and has to be calculated with account of their interaction – as will do later in this section. On the other hand, the second term in Eq. (92) presents *fluctuations* of the environment, which exist even in the absence of system s . Hence, in the first nonvanishing approximation in the interaction strength, the fluctuation part may be calculated ignoring the interaction, i.e. treating the environment as being in the thermodynamic equilibrium:³⁸

$$i\hbar\dot{\tilde{F}} = [\tilde{F}, \hat{H}_e|_{\text{eq}}]. \quad (7.93)$$

Since in this approximation the environment's Hamiltonian does not have an explicit dependence of time, the solution of this equation may be written combining Eqs. (4.175) and (4.190):

$$\hat{F}(t) = \exp\left\{\frac{i}{\hbar} \hat{H}_e|_{\text{eq}} t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e|_{\text{eq}} t\right\}. \quad (7.94)$$

Let us use this relation to calculate the correlation function of fluctuations, defined similarly to Eq. (80), but paying close attention to the order of the time arguments (very soon we will see why):

$$\langle \tilde{F}(t) \tilde{F}(t') \rangle = \left\langle \exp\left\{\frac{i}{\hbar} \hat{H}_e t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t\right\} \exp\left\{\frac{i}{\hbar} \hat{H}_e t'\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t'\right\} \right\rangle, \quad (7.95)$$

where the thermal equilibrium of environment is implied. We are at will to calculate this expectation value in any basis, and the best choice is evident, because in the environment's stationary state basis, its Hamiltonian, the exponents in Eq. (95), and the density operator of the environment are all represented by diagonal matrices. Using Eq. (5), the correlation function becomes

$$\begin{aligned} \langle \tilde{F}(t) \tilde{F}(t') \rangle &= \text{Tr} \left[\hat{w} \exp\left\{\frac{i}{\hbar} \hat{H}_e t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t\right\} \exp\left\{\frac{i}{\hbar} \hat{H}_e t'\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t'\right\} \right] \\ &= \sum_n \left[\hat{w} \exp\left\{\frac{i}{\hbar} \hat{H}_e t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t\right\} \exp\left\{\frac{i}{\hbar} \hat{H}_e t'\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t'\right\} \right]_{nn} \\ &= \sum_{n,n'} W_n \exp\left\{\frac{i}{\hbar} E_n t\right\} \hat{F}_{nn'} \exp\left\{-\frac{i}{\hbar} E_n t\right\} \exp\left\{\frac{i}{\hbar} E_n t'\right\} \hat{F}_{n'n} \exp\left\{-\frac{i}{\hbar} E_n t'\right\} \\ &= \sum_{n,n'} W_n |F_{nn'}|^2 \exp\left\{i \frac{(E_n - E_{n'})(t - t')}{\hbar}\right\}, \quad \text{where } \tilde{E} \equiv E_n - E_{n'}. \end{aligned} \quad (7.96)$$

Here W_n are the Gibbs distribution probabilities, given by Eq. (23) with environment's temperature T , and $F_{nn'}$ are the Schrödinger-picture matrix elements of the interaction force operator.

We see that correlator (96) is a function of the difference $\tau \equiv t - t'$ only (as it should be for fluctuations in a macroscopically stationary system), but may depend on the order of the operands. This is why let us denote this particular correlation function by upper index “+”,

³⁸ Here we assume that for the equilibrium, Eq. (92) has zero average, because if this is not so, this average part of force may be always included into the Hamiltonian of subsystem s .

$$K_F^+(\tau) \equiv \langle \tilde{F}(t) \tilde{F}(t') \rangle = \sum_{n,n'} W_n |F_{nn'}|^2 \exp\left\{i \frac{\tilde{E} \tau}{\hbar}\right\}, \quad \text{where } \tilde{E} \equiv E_n - E_{n'}, \quad (7.97)$$

and its counterpart by upper index “-”:

$$K_F^-(\tau) \equiv K_F^+(-\tau) = \langle \tilde{F}(t') \tilde{F}(t) \rangle = \sum_{n,n'} W_n |F_{nn'}|^2 \exp\left\{-i \frac{\tilde{E} \tau}{\hbar}\right\}. \quad (7.98)$$

Correlation
functions
of an
operator

So, in contrast with classical processes, in quantum mechanics the correlation function of fluctuations $\tilde{F}$ is not necessarily time-symmetric:

$$K_F^+(\tau) - K_F^-(\tau) \equiv K_F^+(\tau) - K_F^+(-\tau) = \langle \tilde{F}(t) \tilde{F}(t') - \tilde{F}(t') \tilde{F}(t) \rangle = 2i \sum_{n,n'} W_n |F_{nn'}|^2 \sin \frac{\tilde{E} \tau}{\hbar} \neq 0, \quad (7.99)$$

so that $\hat{F}(t)$ gives a good example of a Heisenberg-picture operator whose “values”, taken in different moments of time, generally do not commute – the opportunity already mentioned in Sec. 4.6.³⁹

Now let us return to the force decomposition (92), and calculate the first (average) component of the force. In order to do that, let us write the formal solution of Eq. (91) as follows:

$$\hat{F}(t) = \frac{1}{i\hbar} \int_{-\infty}^t [\hat{F}(t'), \hat{H}_e(t')] dt'. \quad (7.100)$$

In the right-hand part of this relation, we cannot treat the Hamiltonian of the environment as an unperturbed (equilibrium) one, because the result would have zero statistical average. Hence, we should make one more step in our perturbative treatment, and take into account (in the first nonvanishing approximation) the effect of our system of interest (s) on the environment. To do this, let us write the (so far, exact) Heisenberg equation of motion for the environment’s Hamiltonian,

$$i\hbar \dot{\hat{H}}_e = [\hat{H}_e, \hat{H}] = -\hat{x} [\hat{H}_e, \hat{F}], \quad (7.101)$$

and its formal solution, similar to Eq. (100), but for an arbitrary time t' rather than t :

$$\hat{H}_e(t') = -\frac{1}{i\hbar} \int_{-\infty}^{t'} \hat{x}(t'') [\hat{H}_e(t''), \hat{F}(t'')] dt''. \quad (7.102)$$

Plugging this equality into the right-hand part of Eq. (100), and averaging the result (again, over the environment only!), we get

$$\langle \hat{F}(t) \rangle = \frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \hat{x}(t'') \langle [\hat{F}(t'), [\hat{H}_e(t''), \hat{F}(t'')]] \rangle. \quad (7.103)$$

As we will see imminently, this expression gives a nonvanishing result even if the right-hand-part averaging is carried over the unperturbed (thermal-equilibrium) environment, so that unless we are interested in higher-order corrections, there is no need to refine the result any further. This fact enables us to calculate the average in the right-hand part of Eq. (103) absolutely similarly to that in Eq. (96), using Eq. (94):

³⁹ A good sanity check here is that at $\tau = 0$, the difference (99) between $K_F(\tau)$ and $K_F(-\tau)$ vanishes.

$$\begin{aligned}
\langle [\hat{F}(t'), [\hat{H}_e(t''), \hat{F}(t'')]] \rangle &= \text{Tr} \{ \mathbf{w} [F(t'), [H_e F(t'')]] \} \\
&= \text{Tr} \{ \mathbf{w} [F(t') H_e F(t'') - F(t') F(t'') H_e - H_e F(t'') F(t') + F(t'') H_e F(t')] \} \\
&= \sum_{n, n'} W_n [F_{nn'}(t') E_{n' n''}(t'') - F_{nn'}(t') F_{n'' n'}(t'') E_n - E_n F_{nn'}(t'') F_{n'' n'}(t') + F_{nn'}(t'') E_{n' n''}(t'')] \\
&= - \sum_{n, n'} W_n \tilde{E} |F_{nn'}|^2 \left[\exp \left\{ i \frac{\tilde{E}}{\hbar} (t' - t'') \right\} + \text{c.c.} \right]. \tag{7.104}
\end{aligned}$$

Now, if we try to integrate each term of this sum, as Eq. (103) seems to require, we will see that the lower-limit substitution (at $t', t'' \rightarrow -\infty$) is uncertain, because the exponents oscillate without decay. This technical difficulty may be overcome by the following reasoning. As illustrated by the example considered in the previous section, coupling to a disordered environment makes the “memory horizon” of the subsystem of our interest (s) finite: its current state does not depend on its history beyond certain time scale – in that example, the dephasing time T_2 . (Actually, this is true for virtually all real physical systems, in contrast to the idealized models such as a dissipation-free pendulum that swings for ever and ever with the same amplitude.) As a result, the functions under integrals of Eq. (103), i.e. the sum (104), should self-average at a certain finite time. One simple technique for expressing this fact mathematically is just dropping the lower-limit substitution; this would give the correct result for Eq. (103). However, a better (mathematically more acceptable) trick is to first multiply the function under each integral by, respectively, $\exp\{\varepsilon(t - t')\}$ and $\exp\{\varepsilon(t - t'')\}$, where ε is a very small positive constant, then carry out the integration, and after that take the limit $\varepsilon \rightarrow 0$. The physical justification of this procedure may be provided by saying that system’s behavior should not be affected if its interaction with the environment was not kept constant but was turned on gradually – say, exponentially with an infinitesimal rate ε . With this modification, Eq. (103) becomes

$$\langle \hat{F}(t) \rangle = -\frac{1}{\hbar^2} \sum_{n, n'} W_n \tilde{E} |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \hat{x}(t'') \left[\exp \left\{ i \frac{\tilde{E}}{\hbar} (t' - t'') + \varepsilon(t'' - t) \right\} + \text{c.c.} \right]. \tag{7.105}$$

This double integration is over the area shaded in Fig. 6, so that the order of integration may be changed to the opposite one as

$$\int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \dots = \int_{-\infty}^t dt'' \int_{t''}^t dt' \dots = \int_{-\infty}^t dt'' \int_0^{\tau} d\tau' \dots, \tag{7.106}$$

where $\tau' \equiv t - t'$, and $\tau \equiv t - t''$.

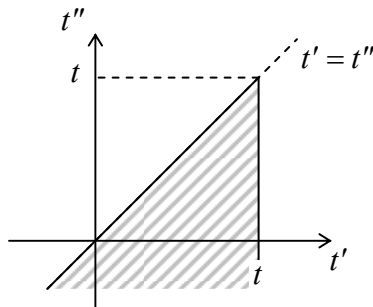


Fig. 7.6. 2D integration area in Eqs. (105) and (106).

As a result, Eq. (105) may be rewritten as a single integral,

$$\langle \hat{F}(t) \rangle = \int_{-\infty}^t G(t-t'') \hat{x}(t'') dt'' = \int_0^{\infty} G(\tau) \hat{x}(t-\tau) d\tau, \quad (7.107)$$

Ensemble
average of
environment's
response

whose kernel,

$$\begin{aligned} G(\tau > 0) &= -\frac{1}{\hbar^2} \sum_{n,n'} W_n \tilde{E} |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \int_0^{\tau} \exp \left\{ i \frac{\tilde{E}}{\hbar} (\tau - \tau') - \varepsilon \tau \right\} + \text{c.c.} \Big] d\tau' \\ &= \lim_{\varepsilon \rightarrow 0} \frac{2}{\hbar} \sum_{n,n'} W_n |F_{nn'}|^2 \sin \frac{\tilde{E}\tau}{\hbar} e^{-\varepsilon\tau} = \frac{2}{\hbar} \sum_{n,n'} W_n |F_{nn'}|^2 \sin \frac{\tilde{E}\tau}{\hbar}, \end{aligned} \quad (7.108)$$

does not depend on the particular law of evolution of the subsystem (s) under study, i.e. provides a general characterization of its coupling to the environment.

In Eq. (107) we may readily recognize the most general form of the linear response of a system (in our case, the environment), taking into account the causality principle, where $G(\tau)$ is the *response function* (also called the “temporal Green’s function”) of the environment.⁴⁰ Comparing Eq. (108) with Eq. (99), we get a wonderfully simple universal relation,⁴¹

$$\left\langle \left[\hat{F}(\tau), \hat{F}(0) \right] \right\rangle = i\hbar G(\tau). \quad (7.109)$$

Fluctuation
commutator
via Green's
function

that emphasizes once again the quantum nature of the correlation function’s time asymmetry. However, the relation between $G(\tau)$ and the force *anti*-commutator,

$$\left\langle \left\{ \hat{F}(t+\tau), \hat{F}(t) \right\} \right\rangle \equiv \left\langle \hat{F}(t+\tau) \hat{F}(t) + \hat{F}(t) \hat{F}(t+\tau) \right\rangle = K_F^+(\tau) + K_F^-(\tau), \quad (7.110)$$

is much more important because of the following reason. Relations (97)-(98) show that the so-called *symmetrized correlation function*,

$$\begin{aligned} K_F(\tau) &\equiv \frac{K_F^+(\tau) + K_F^-(\tau)}{2} = \frac{1}{2} \left\langle \left\{ \hat{F}(\tau), \hat{F}(0) \right\} \right\rangle = \lim_{\varepsilon \rightarrow 0} \sum_{n,n'} W_n |F_{nn'}|^2 \cos \frac{\tilde{E}\tau}{\hbar} e^{-2\varepsilon|\tau|} \\ &= \sum_{n,n'} W_n |F_{nn'}|^2 \cos \frac{\tilde{E}\tau}{\hbar}, \end{aligned} \quad (7.111)$$

Symmetrized
correlation
function

that is evidently an even function of time difference τ , looks very similar to the response function (108), “only” with another trigonometric function under the sum. This similarity may be used to obtain an exact algebraic relation between the Fourier images of these two functions of τ . Indeed, function (111) may be represented as the Fourier transform⁴²

⁴⁰ For a more detailed discussion of this function and the causality principle, see, e.g., CM Sec. 4.1.

⁴¹ This relation, called the *Kubo* (or “Green-Kubo”) *formula*, after the works by M. Green (1954) and R. Kubo (1957), does not come up in the easier derivations of the FDT, discussed in the beginning of this section.

⁴² Due to their practical importance, and certain mathematical issues with their justification for random functions, Eqs. (112)-(113) have their own grand name, the *Wiener-Khinchin theorem*, though the math rigor aside, they are just a straightforward corollary of the Fourier integral transform (115) – see, e.g., SM Sec. 5.4.

$$K_F(\tau) = \int_{-\infty}^{+\infty} S_F(\omega) e^{-i\omega\tau} d\omega = 2 \int_0^{+\infty} S_F(\omega) \cos \omega\tau d\omega, \quad (7.112)$$

with the reciprocal transform

$$S_F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} K_F(\tau) e^{i\omega\tau} d\tau = \frac{1}{\pi} \int_0^{+\infty} K_F(\tau) \cos \omega\tau d\tau. \quad (7.113)$$

via the *symmetrized spectral density* of variable F , defined as

Symmetrized
spectral
density

$$S_F(\omega) \delta(\omega - \omega') \equiv \frac{1}{2} \langle \hat{F}_\omega \hat{F}_{-\omega'} + \hat{F}_{-\omega'} \hat{F}_\omega \rangle = \frac{1}{2} \langle \{ \hat{F}_\omega, \hat{F}_{-\omega'} \} \rangle, \quad (7.114)$$

where $\hat{F}_\omega$ (also an operator rather than a c -number!) is defined as

$$\hat{F}_\omega \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} \hat{F}(t) e^{i\omega t} dt, \quad \text{so that} \quad \hat{F}(t) = \int_{-\infty}^{+\infty} \hat{F}_\omega e^{-i\omega t} d\omega. \quad (7.115)$$

The physical meaning of function $S_F(\omega)$ becomes evident if we write Eq. (112) for the particular case $\tau = 0$:

$$K_F(0) \equiv \langle \hat{F}^2 \rangle = \int_{-\infty}^{+\infty} S_F(\omega) d\omega = 2 \int_0^{+\infty} S_F(\omega) d\omega. \quad (7.116)$$

This formula implies that if we pass function $F(t)$ through a linear filter cutting from its frequency spectrum a narrow band $d\omega$ of real (positive) frequencies, then variance $\langle F_f^2 \rangle$ of the filtered signal $F_f(t)$ would be equal to $2S_F(\omega)d\omega$ – hence the name “spectral density”.⁴³

Let us use Eqs. (111) and (113) to calculate the spectral density for our model:

$$\begin{aligned} S_F(\omega) &= \sum_{n,n'} W_n |F_{nn'}|^2 \frac{1}{2\pi} \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{+\infty} \cos \frac{\tilde{E}\tau}{\hbar} e^{-\varepsilon|\tau|} e^{i\omega\tau} d\tau \\ &= \frac{1}{2\pi} \sum_{n,n'} W_n |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \int_0^{+\infty} \left[\exp \left\{ i \frac{\tilde{E}\tau}{\hbar} \right\} + \text{c.c.} \right] e^{-\varepsilon\tau} e^{i\omega\tau} d\tau \\ &= \frac{1}{2\pi} \sum_{n,n'} W_n |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \left[\frac{1}{i(\tilde{E}/\hbar + \omega) - \varepsilon} + \frac{1}{i(-\tilde{E}/\hbar + \omega) - \varepsilon} \right]. \end{aligned} \quad (7.117)$$

Now it is a convenient time to recall that each of the two summations here is over the eigenenergy spectrum of the environment whose spectrum is virtually continuous because of its large size, so that we may transform each sum into an integral just as this was done in Sec. 6.6:

$$\sum_n \dots \rightarrow \int \dots dn = \int \dots \rho(E_n) dE_n, \quad (7.118)$$

⁴³ An alternative popular measure of spectral density is $\mathcal{S}_F(\nu) \equiv \langle F_f^2 \rangle / d\nu = 4\pi S_F(\omega)$, where $\nu = \omega/2\pi$ is the “cyclic” frequency (measured in Hz).

where $\rho(E)$ is the density of environment's states at a given energy. This transformation yields

$$S_F(\omega) = \frac{1}{2\pi} \lim_{\varepsilon \rightarrow 0} \int dE_n W(E_n) \rho(E_n) \int dE_{n'} \rho(E_{n'}) |F_{nn'}|^2 \left[\frac{1}{i(\tilde{E}/\hbar - \omega) - \varepsilon} + \frac{1}{i(-\tilde{E}/\hbar - \omega) - \varepsilon} \right]. \quad (7.119)$$

Since the square bracket depends only on a specific linear combination of two energies, $\tilde{E} \equiv E_n - E_{n'}$, it is convenient to introduce also another, linearly-independent combination of the energies, for example, the average energy $\bar{E} = (E_n + E_{n'})/2$, so that the state energies may be presented as

$$E_n = \bar{E} + \frac{\tilde{E}}{2}, \quad E_{n'} = \bar{E} - \frac{\tilde{E}}{2}. \quad (7.120)$$

With this notation, Eq. (119) becomes

$$S_F(\omega) = -\frac{\hbar}{2\pi} \lim_{\varepsilon \rightarrow 0} \int d\bar{E} \left[\int W\left(\bar{E} + \frac{\tilde{E}}{2}\right) \rho\left(\bar{E} + \frac{\tilde{E}}{2}\right) \rho\left(\bar{E} - \frac{\tilde{E}}{2}\right) |F_{nn'}|^2 \frac{d\tilde{E}}{i(\tilde{E} - \hbar\omega) - \hbar\varepsilon} \right. \\ \left. + \int W\left(\bar{E} + \frac{\tilde{E}}{2}\right) \rho\left(\bar{E} + \frac{\tilde{E}}{2}\right) \rho\left(\bar{E} - \frac{\tilde{E}}{2}\right) |F_{nn'}|^2 \frac{d\tilde{E}}{i(-\tilde{E} - \hbar\omega) - \hbar\varepsilon} \right]. \quad (7.121)$$

Due to the smallness of parameter $\hbar\varepsilon$ (which should be much less than all real energies, including $k_B T$, $\hbar\omega$, E_n , and $E_{n'}$), each of the internal integrals is dominated by an infinitesimal vicinity of one point, $\tilde{E}_{\pm} = \pm\hbar\omega$, in which the spectral density, matrix elements, and the Gibbs probabilities do not change considerably, and may be taken out of the integrals, so that they may be worked out explicitly:⁴⁴

$$S_F(\omega) = -\frac{\hbar}{2\pi} \lim_{\varepsilon \rightarrow 0} \int d\bar{E} \rho_+ \rho_- \left[W_+ |F_+|^2 \int_{-\infty}^{+\infty} \frac{d\tilde{E}}{i(\tilde{E} - \hbar\omega) - \hbar\varepsilon} + W_- |F_-|^2 \int_{-\infty}^{+\infty} \frac{d\tilde{E}}{i(-\tilde{E} - \hbar\omega) - \hbar\varepsilon} \right] \\ = -\frac{\hbar}{2\pi} \lim_{\varepsilon \rightarrow 0} \int d\bar{E} \rho_+ \rho_- \left[W_+ |F_+|^2 \int_{-\infty}^{+\infty} \frac{-i(\tilde{E} - \hbar\omega) - \hbar\varepsilon}{(\tilde{E} - \hbar\omega)^2 + (\hbar\varepsilon)^2} d\tilde{E} + W_- |F_-|^2 \int_{-\infty}^{+\infty} \frac{i(\tilde{E} + \hbar\omega) - \hbar\varepsilon}{(\tilde{E} + \hbar\omega)^2 + (\hbar\varepsilon)^2} d\tilde{E} \right] \quad (7.122) \\ = \frac{\hbar}{2} \int \rho_+ \rho_- [W_+ |F_+|^2 + W_- |F_-|^2] d\bar{E},$$

where indices $\pm$ mark function values at the special points $\tilde{E}_{\pm} = \pm\hbar\omega$, i.e. $E_n = E_{n'} \pm \hbar\omega$. The physics of these points becomes simple if we interpret state n , that is the argument of the equilibrium Gibbs distribution function W_n , as the initial state of the environment, and n' as its finite state. Then the top-sign point corresponds to $E_{n'} = E_n - \hbar\omega$, i.e. to the emission of one energy quantum $\hbar\omega$ of the “observation” frequency ω by the environment into subsystem s of interest, while the bottom-sign point $E_{n'} = E_n + \hbar\omega$, corresponds to the absorption of such quantum by the environment. As Eq. (122) shows, both processes give similar positive contributions into force fluctuations.

⁴⁴ Using, e.g., MA Eq. (6.5a). (The imaginary parts of the integrals vanish, because integration in infinite limits may be always re-centered to finite points $\pm\hbar\omega$.) A mathematically enlightened reader may have noticed that the integrals might be taken without the introduction of small ε , using the Cauchy theorem – see MA Eq. (15.1).

The situation is different for the Fourier image of the response function $G(\tau)$,⁴⁵

$$\chi(\omega) \equiv \int_0^{+\infty} G(\tau) e^{i\omega\tau} d\tau, \quad (7.123)$$

Generalized
susceptibility

that is frequently called either the *generalized susceptibility* or the *response function* - in our case, of the environment. Its physical meaning is that the complex function $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ relates the Fourier amplitudes of the generalized coordinate and generalized force:⁴⁶

$$\langle \hat{F}_\omega \rangle = \chi(\omega) \hat{x}_\omega. \quad (7.124)$$

The physics of its imaginary part $\chi''(\omega)$ is especially clear. Indeed, if both F_ω and x_ω represent a sinusoidal classical process, say

$$x(t) = x_0 \cos \omega t = \frac{x_0}{2} e^{-i\omega t} + \frac{x_0}{2} e^{+i\omega t}, \quad \text{i.e. } x_\omega = x_{-\omega} = \frac{x_0}{2}, \quad (7.125)$$

Then, in accordance with the correspondence principle, Eq. (124) should hold for the *c*-number complex amplitudes F_ω and x_ω , enabling us to calculate the time dependence of force,

$$\begin{aligned} F(t) &= F_\omega e^{-i\omega t} + F_{-\omega} e^{+i\omega t} = \chi(\omega) x_\omega e^{-i\omega t} + \chi(-\omega) x_{-\omega} e^{+i\omega t} = \frac{x_0}{2} [\chi(\omega) e^{-i\omega t} + \chi(-\omega) e^{+i\omega t}] \\ &= \frac{x_0}{2} [(\chi' + i\chi'') e^{-i\omega t} + (\chi' - i\chi'') e^{+i\omega t}] = x_0 [\chi'(\omega) \cos \omega t - \chi''(\omega) \sin \omega t] \end{aligned} \quad (7.126)$$

We see that $\chi''(\omega)$ scales the part of the force that is $\pi/2$ -shifted from the coordinate oscillations, i.e. is in phase with those of velocity, and hence characterizes the time-average power flow from the system into the environment, i.e. the *energy dissipation rate*.⁴⁷

$$\bar{P} = \overline{F(t)\dot{x}(t)} = x_0 [\chi'(\omega) \cos \omega t - \chi''(\omega) \sin \omega t] (-\omega x_0 \sin \omega t) = \frac{x_0^2}{2} \omega \chi''(\omega). \quad (7.127)$$

Let us calculate this function from Eqs. (108) and (123), just as we have done for the spectral density of fluctuations:

$$\begin{aligned} \chi''(\omega) &= \text{Im} \int_0^{+\infty} G(\tau) e^{i\omega\tau} d\tau = \frac{2}{\hbar} \sum_{n,n'} W_n |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \text{Im} \int_0^{+\infty} \frac{1}{2i} \left(\exp \left\{ i \frac{\tilde{E}\tau}{\hbar} \right\} - \text{c.c.} \right) e^{i\omega\tau} e^{-\varepsilon\tau} d\tau \\ &= \sum_{n,n'} W_n |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \text{Im} \left(\frac{1}{-\tilde{E} - \hbar\omega - i\hbar\varepsilon} - \frac{1}{\tilde{E} - \hbar\omega - i\hbar\varepsilon} \right) \end{aligned}$$

⁴⁵ Integration in Eq. may be extended to the whole time axis, $-\infty < \tau < +\infty$, if we complement definition (107) of $G(\tau)$ for $\tau > 0$ with its definition as $G(\tau) = 0$ for $\tau < 0$, in correspondence with the causality principle.

⁴⁶ In order to prove this relation, it is sufficient to plug expression $\hat{x}_s = \hat{x}_\omega e^{-i\omega t}$, or any sum of such exponents, into Eqs. (107) and then use definition (123). This simple exercise is highly recommended to the reader.

⁴⁷ The expression $P = F\dot{x} = Fv$ used for the instant power flow is evident if x is the usual Cartesian coordinate of a mechanical system. According to analytical mechanics (see, e.g., CM Chapters 2 and 10), it is valid for any generalized coordinate – generalized force pair which forms the interaction Hamiltonian (90).

$$= \sum_{n,n'} W_n |F_{nn'}|^2 \lim_{\varepsilon \rightarrow 0} \left(\frac{\hbar \varepsilon}{(\tilde{E} + \hbar \omega)^2 + (\hbar \varepsilon)^2} - \frac{\hbar \varepsilon}{(\tilde{E} - \hbar \omega)^2 + (\hbar \varepsilon)^2} \right). \quad (7.128)$$

Making the transfer (118) from the double sum to the double integral, and then the integration variable transfer (120), we get

$$\begin{aligned} \chi''(\omega) = \lim_{\varepsilon \rightarrow 0} \int d\tilde{E} & \left[\int_{-\infty}^{+\infty} W \left(\bar{E} + \frac{\tilde{E}}{2} \right) \rho \left(\bar{E} + \frac{\tilde{E}}{2} \right) \rho \left(\bar{E} - \frac{\tilde{E}}{2} \right) |F_{nn'}|^2 \frac{\hbar \varepsilon}{(\tilde{E} + \hbar \omega)^2 + (\hbar \varepsilon)^2} d\tilde{E} \right. \\ & \left. - \int_{-\infty}^{+\infty} W \left(\bar{E} + \frac{\tilde{E}}{2} \right) \rho \left(\bar{E} + \frac{\tilde{E}}{2} \right) \rho \left(\bar{E} - \frac{\tilde{E}}{2} \right) |F_{nn'}|^2 \frac{\hbar \varepsilon}{(\tilde{E} - \hbar \omega)^2 + (\hbar \varepsilon)^2} d\tilde{E} \right]. \end{aligned} \quad (7.129)$$

Now using the same argument about the smallness of parameter ε as above, we may take the spectral densities, matrix elements of force, and the Gibbs probabilities out of the integrals, and work out the integrals, getting a result very similar to Eq. (122):

$$\chi''(\omega) = \pi \int \rho_+ \rho_- [W_- |F_-|^2 - W_+ |F_+|^2] d\bar{E}. \quad (7.130)$$

In order to relate these results, it is sufficient to notice that according to Eq. (23), the Gibbs probabilities $W_{\pm}$ are related by coefficients dependent on only the temperature T and observation frequency ω :

$$W_{\pm} \equiv W \left(\bar{E} + \frac{\tilde{E}_{\pm}}{2} \right) \equiv W \left(\bar{E} \pm \frac{\hbar \omega}{2} \right) = \frac{1}{Z} \exp \left\{ -\frac{\bar{E} \pm \hbar \omega / 2}{k_B T} \right\} = W(\bar{E}) \exp \left\{ \mp \frac{\hbar \omega}{2 k_B T} \right\}, \quad (7.131)$$

so that both the spectral density and the dissipative part of susceptibility may expressed via the same integral over environment energies:

$$S_F(\omega) = \hbar \cosh \left(\frac{\hbar \omega}{2 k_B T} \right) \int \rho_+ \rho_- W(\bar{E}) [|F_+|^2 + |F_-|^2] d\bar{E}, \quad (7.132)$$

$$\chi''(\omega) = 2\pi \sinh \left(\frac{\hbar \omega}{2 k_B T} \right) \int \rho_+ \rho_- W(\bar{E}) [|F_+|^2 + |F_-|^2] d\bar{E}, \quad (7.133)$$

and hence are universally related as

$$S_F(\omega) = \frac{\hbar}{2\pi} \chi''(\omega) \coth \frac{\hbar \omega}{2 k_B T}. \quad (7.134)$$

Fluctuation-
dissipation
theorem

This is the Callen-Welton's fluctuation-dissipation theorem (FDT). It reveals the fundamental, intimate relation between dissipation and fluctuations induced by environment ("no dissipation without fluctuations") – hence the name.⁴⁸ In the classical limit, $\hbar \omega \ll k_B T$, the FDT is reduced to

⁴⁸ A curious feature of the FDT is that Eq. (134) includes the exactly same function of temperature as the average energy (26) of a quantum oscillator of frequency ω , though, as the reader could witness, the notion of the

$$S_F(\omega) = \frac{\hbar}{2\pi} \chi''(\omega) \frac{2k_B T}{\hbar \omega} = \frac{k_B T}{\pi} \frac{\text{Im} \chi(\omega)}{\omega}. \quad (7.135)$$

In most systems of interest the last fraction tends to a finite (positive) constant in a substantial range of relatively low frequencies. Indeed, expanding Eq. (123) in the Taylor series in small ω , we get

$$\chi(\omega) = \chi(0) + i\omega\eta + \dots, \quad \text{with } \chi(0) = \int_0^\infty G(\tau) d\tau, \quad \text{and } \eta \equiv \int_0^\infty G(\tau) \tau d\tau. \quad (7.136)$$

Since the temporal Green's function is real by definition, the Taylor expansion of $\chi''(\omega) \equiv \text{Im} \chi(\omega)$ starts with the linear term $i\omega\eta$, where η is a certain real coefficient, and unless $\eta = 0$, is dominated by this term at small ω . (The physical sense of constant η becomes clear if we consider an environment that provides viscous friction with the simple law

$$\langle \hat{F} \rangle = -\eta \dot{x}, \quad \eta \geq 0. \quad (7.137)$$

Viscosity
coefficient

For the Fourier images of coordinate and force this gives the relation $F_\omega = i\alpha x_\omega$, so that according to Eq. (124),

$$\chi(\omega) = i\omega\eta, \quad \text{i.e. } \frac{\chi''(\omega)}{\omega} \equiv \frac{\text{Im} \chi(\omega)}{\omega} = \eta \geq 0. \quad (7.138)$$

Hence, even in the general case, coefficient η may be considered as an effective low-speed *viscosity* provided by the environment.)

In this case Eq. (134) turns into the *Nyquist formula*:⁴⁹

Nyquist
formula

$$S_F(\omega) = \frac{k_B T}{\pi} \eta, \quad \text{i.e. } \langle F_f^2 \rangle = 4k_B T \eta d\nu. \quad (7.139)$$

According to Eq. (112), if such a constant spectral density⁵⁰ persisted at all frequencies, it would correspond to a delta-correlated process $F(t)$, with

$$K_F(\tau) = 2\pi S_F(0) \delta(\tau) = 2k_B T \eta \delta(\tau), \quad (7.140)$$

similar to already discussed above – see Eq. (82).

oscillator was by no means used in its derivation. As will see in the next section, this fact leads to rather interesting consequences and even conceptual opportunities.

⁴⁹ Actually, the 1928 work by H. Nyquist was about electronic noise in resistors, just discovered experimentally by his Bell Labs colleague J. Johnson. For an Ohmic resistor, as a dissipative “environment” of the electric circuit it is connected with, Eq. (137) is just the Ohm's law, and may be recast as either $\langle V \rangle = -R(dQ/dt) = RI$, or $\langle I \rangle = -G(d\Phi/dt) = GV$. Thus for voltage V in an open circuit, η corresponds to resistance R , while for current I in the short circuit, to conductance $G = 1/R$. In this case, the fluctuations described by Eq. (139) are referred to as the *Johnson-Nyquist noise*. (Because of this important application, any model leading to Eqs. (136)-(137) is frequently referred to as *Ohmic dissipation*, even if the physical nature of variables x and F is quite different.) Another note: the Nyquist formula (139) should not be confused with the *Nyquist-Shannon theorem* describing the minimum sampling rate of an analog signal.

⁵⁰ A random process whose properties may be reasonably approximated by constant spectral density is frequently called the *white noise*, because then it is a random mixture of all possible sinusoidal components with equal weights, reminding natural white light's composition.

Since in the classical limit the right-hand part of Eq. (109) is negligible, and the correlation function may be considered an even function of time, the symmetrized function under the integral in Eq. (113) may be rewritten just as $\langle F(\tau)F(0) \rangle$. In the limit of low observation frequencies (in the sense that ω is much smaller than not only the quantum frontier $k_B T/\hbar$, but also the frequency scale of function $\chi''(\omega)/\omega$), Eq. (138) may be used to recast Eq. (135) in the form⁵¹

$$\eta \equiv \lim_{\omega \rightarrow 0} \frac{\chi''(\omega)}{\omega} = \frac{1}{k_B T} \int_0^\infty \langle F(\tau)F(0) \rangle d\tau. \quad (7.141)$$

To conclude this section, let me return for a minute to the questions formulated in our earlier discussion of dephasing in the two-level model. In that problem, the dephasing time scale is $T_2 = 1/2D_\phi$. Hence the classical approach to the environment, used in Sec. 3, is adequate if $\hbar D_\phi \ll k_B T$. Next, we may identify operators $\hat{f}$ and $\hat{\sigma}_z$ participating in Eq. (70) with, respectively, operators $\hat{F}$ and $\hat{x}$ of the general Eq. (90). Then the comparison of Eqs. (82), (88) and (140) yields

$$\frac{1}{T_2} = 2D_\phi = \frac{4k_B T}{\hbar^2} \eta, \quad (7.142)$$

Dephasing
time via
viscosity

so that, for the model described by Eq. (137) with temperature-independent viscosity η , the dephasing rate is proportional to temperature.

7.5. The Heisenberg-Langevin approach

The fluctuation-dissipation theorem opens a very simple and efficient way for analysis of the system of interest (s in Fig. 1). It is to write its Heisenberg equations (4.199) of motion for relevant operators, which would now include the environmental force operator, and explore these equations using the Fourier transform and the Wiener-Khinchin theorem (112)-(113). Such approach to classical equations of motion is commonly associated with the name of Langevin,⁵² so that its extension to dynamics of Heisenberg-picture operators is frequently referred to as the *Heisenberg-Langevin* (or “quantum Langevin”) *approach* to open system analysis.⁵³

Perhaps the best way to describe this method is to demonstrate how it works for the very important case of a 1D harmonic oscillator, so that the generalized coordinate x of Sec. 4 is just the oscillator’s coordinate. For the sake of simplicity, let us assume that the environment provides the simple Ohmic dissipation described by Eq. (137) - which is a good approximation in many cases. As we already know from Chapter 5, the Heisenberg equations of motion for operators of coordinate and momentum of the oscillator, in the presence of external force, are

⁵¹ In some fields (especially in physical kinetics and chemical physics), this particular limit of the Nyquist formula, is called the *Green-Kubo* (or just “Kubo”) *formula*. As was discussed above, these names may be more reasonably associated with Eq. (109).

⁵² After P. Langevin, whose 1908 work was the first systematic development of Einstein’s ideas (1905) of the Brownian motion theory in the random force language, as an alternative to M. Smoluchowski’s approach using the probability density language – see Sec. 6 below.

⁵³ Perhaps the largest credit for this extension belongs to M. Lax whose work, in the early 1960s, was motivated mostly by quantum electronics applications – see, e.g., his monograph M. Lax, *Fluctuation and Coherent Phenomena in Classical and Quantum Physics*, Gordon and Breach, 1968, and references therein.

$$\dot{\hat{x}} = \frac{\hat{p}}{m}, \quad \dot{\hat{p}} = -m\omega_0^2 \hat{x} + \hat{F}, \quad (7.143)$$

so that using Eqs. (92) and (137), we get

$$\dot{\hat{x}} = \frac{\hat{p}}{m}, \quad \dot{\hat{p}} = -m\omega_0^2 \hat{x} - \eta \dot{\hat{x}} + \hat{\tilde{F}}(t). \quad (7.144)$$

Combining Eqs. (144), we may write their system as a single differential equation

$$m\ddot{\hat{x}} + \eta \dot{\hat{x}} + m\omega_0^2 \hat{x} = \hat{\tilde{F}}(t), \quad (7.145)$$

that is absolutely similar to the classical equation of motion.⁵⁴ (In the view of Eqs. (5.42) and (5.48), whose corollary the Ehrenfest theorem (5.49) is, this should be by no means surprising.) For the Fourier images of the operators, defined similarly to Eq. (115), Eq. (145) gives the following relation,

$$\hat{x}_\omega = \frac{\hat{F}_\omega}{m(\omega_0^2 - \omega^2) - i\eta\omega}, \quad (7.146)$$

that should be also well known to the reader from the classical theory of forced oscillations. However, since the Fourier components are still Heisenberg-picture operators, and their “values” for different ω do not commute, we have to tread carefully. The best way to proceed is to write a copy of Eq. (146) for frequency $(-\omega)$, and then combine these equations to form a symmetrical combination similar that used in Eq. (114). The result is

$$\frac{1}{2} \langle \hat{x}_\omega \hat{x}_{-\omega} + \hat{x}_{-\omega} \hat{x}_\omega \rangle = \frac{1}{|m(\omega_0^2 - \omega^2) - i\eta\omega|^2} \frac{1}{2} \langle \hat{F}_\omega \hat{F}_{-\omega} + \hat{F}_{-\omega} \hat{F}_\omega \rangle. \quad (7.147)$$

Since the spectral density definition similar to Eq. (114) is valid for any observable, in particular for x , Eq. (147) allows us to relate the symmetrized spectral densities of coordinate and force:

$$S_x(\omega) = \frac{S_F(\omega)}{|m(\omega_0^2 - \omega^2) - i\eta\omega|^2} = \frac{S_F(\omega)}{m^2(\omega_0^2 - \omega^2)^2 + (\eta\omega)^2}. \quad (7.148)$$

Now using an analog of Eq. (116) for x , we can calculate coordinate's variance:

$$\langle x^2 \rangle = K_x(0) = \int_{-\infty}^{+\infty} S_x(\omega) d\omega = 2 \int_0^{+\infty} \frac{S_F(\omega) d\omega}{m^2(\omega_0^2 - \omega^2)^2 + (\eta\omega)^2}, \quad (7.149)$$

where now, in contrast to the notation used in Sec. 4, sign $\langle \dots \rangle$ means the averaging over the usual statistical ensemble of many systems of interest – in our current case, of many harmonic oscillators.

If the coupling to environment is so weak that viscosity η is small (in the sense that the oscillator's dimensionless *Q-factor*⁴⁸ is large, $Q \equiv m\omega_0/\eta \gg 1$), this integral is dominated by the resonance peak in a narrow vicinity, $|\omega - \omega_0| \equiv |\xi| \ll \omega_0$, of its resonance frequency, and we can take the relatively smooth function $S_F(\omega)$ out of the integral, thus reducing it to a table integral:⁵⁵

⁵⁴ See, e.g., CM Sec. 4.1.

⁵⁵ See, e.g., MA Eq. (6.5a).

$$\begin{aligned}
\langle x^2 \rangle &\approx 2S_F(\omega_0) \int_0^{+\infty} \frac{d\omega}{m^2(\omega_0^2 - \omega^2)^2 + (\eta\omega)^2} \approx 2S_F(\omega_0) \int_{-\infty}^{+\infty} \frac{d\xi}{(2m\omega_0\xi)^2 + (\eta\omega_0)^2} \\
&= 2S_F(\omega_0) \frac{1}{(\eta\omega_0)^2} \int_{-\infty}^{+\infty} \frac{d\xi}{(2m\xi/\eta)^2 + 1} = 2S_F(\omega_0) \frac{1}{(\eta\omega_0)^2} \frac{\pi\eta}{2m} = \frac{\pi}{\eta m \omega_0^2} S_F(\omega_0).
\end{aligned} \tag{7.150}$$

With the account of the FDT (134) and Eq. (138), this gives

$$\langle x^2 \rangle = \frac{\pi}{\eta m \omega_0^2} \frac{\hbar}{2\pi} \eta \omega_0 \coth \frac{\hbar \omega_0}{2k_B T} = \frac{\hbar}{2m \omega_0} \coth \frac{\hbar \omega_0}{2k_B T}. \tag{7.151}$$

But this is exactly Eq. (48) that was obtained from the Gibbs distribution, without any explicit account of the environment - though keeping it in mind by using the notion of the thermally-equilibrium ensemble.⁵⁶ (Notice that the viscosity coefficient η , that characterizes the oscillator-to-environment interaction strength, has cancelled!) Does this mean that we have toiled in vain?

By no means. First of all, the FDT result has an important conceptual value. For example, let us consider the low-temperature limit $k_B T \ll \hbar \omega_0$, when Eq. (151) is reduced to

$$\langle x^2 \rangle = \frac{x_0^2}{2} = \frac{\hbar}{2m \omega_0}. \tag{7.152}$$

Let us ask a naïve question: What exactly is the origin of this coordinate uncertainty? From the point of view of the usual quantum mechanics of closed (Hamiltonian) systems, there is no doubt: this nonvanishing variance of coordinate is the result of the final spatial extension of the ground-state wavefunction, reflecting the Heisenberg's uncertainty relation (that in turn results from the fact that the operators of coordinate and momentum do not commute) – see Eq. (2.271). However, from the point of view of the Heisenberg-Langevin equation (145), variance (152) is an unalienable part of the oscillator's response to the fluctuation force $\tilde{F}(t)$ exerted by the environment at frequencies $\omega \approx \omega_0$. Though it is impossible to refute the former, absolutely legitimate point of view, in many applications it is much easier to subscribe to the latter standpoint, and treat the coordinate uncertainty as the result of the so-called *quantum noise* of the environment. This notion has received numerous confirmations in experiments that did not include *any* oscillators with the eigenfrequencies ω_0 close to the noise measurement frequency ω .⁵⁷

The advantage of the Heisenberg-Langevin approach is that for any $\eta > 0$ it is possible to calculate the (experimentally measurable!) distribution $S_x(\omega)$, i.e. decompose the fluctuations into spectral components. This procedure is not restricted to the limit of small η (large Q factors); for any damping we may just plug the FDT (134) into Eq. (149) and integrate. As an example, let us have a look at the so-called *quantum diffusion*. A free 1D particle may be considered as the particular case of a 1D harmonic oscillator with $\omega_0 = 0$, so that combining Eqs. (134) and (149), we get

⁵⁶ By the way, the simplest way to calculate $S_F(\omega)$, i.e. to derive the FDT, is to *require* that Eqs. (48) and (150) give the same result for an oscillator with any eigenfrequency ω . This is exactly the approach used by H. Nyquist (for the classical case) – see also SM Sec. 5.5.

⁵⁷ See, for example, R. Koch *et al.*, *Phys. Rev. B* **26**, 74 (1982)..

$$\langle x^2 \rangle = 2 \int_0^{+\infty} \frac{S_F(\omega) d\omega}{(m\omega^2)^2 + (\eta\omega)^2} = 2\eta \int_0^{+\infty} \frac{1}{(m\omega^2)^2 + (\eta\omega)^2} \frac{\hbar\omega}{2\pi} \coth \frac{\hbar\omega}{2k_B T} d\omega. \quad (7.153)$$

This integral has two divergences. The first one, of the type $|d\omega/\omega^2|$ at the lower limit, is just a classical effect: according to Eq. (85), particle's displacement variance grows with time, so it cannot have a finite time-independent value that Eq. (153) tries to calculate. However, we still can use that result to single out the quantum noise effect on diffusion - say, by comparing it with a similar but purely classical case. These effects are prominent at high frequencies, especially if the quantum noise overcomes the thermal noise before the dynamic cut-off, i.e. if

$$\frac{k_B T}{\hbar} \ll \frac{\eta}{m}. \quad (7.154)$$

In this case there is a broad range of frequencies where the quantum noise gives a substantial contribution to the integral:

Quantum
diffusion

$$\langle x^2 \rangle_Q \approx 2\eta \int_{k_B T/\hbar}^{\eta/m} \frac{1}{(\eta\omega)^2} \frac{\hbar\omega}{2\pi} d\omega = \frac{\hbar}{\pi\eta} \int_{k_B T/\hbar}^{\eta/m} \frac{d\omega}{\omega} = \frac{\hbar}{\pi\eta} \ln \frac{\hbar\eta}{mk_B T} \sim \frac{\hbar}{\eta}. \quad (7.155)$$

Formally, this contribution diverges at either $m \rightarrow 0$ or $T \rightarrow 0$, but this logarithmic (i.e. extremely weak) divergence is readily quenched by an almost any change of the environment model at very high frequencies, where the “Ohmic” approximation given by Eq. (136) becomes unrealistic.

The Heisenberg-Langevin approach is extremely simple and powerful,⁵⁸ but it has its limitations. The main one is that if the equations of motion for the Heisenberg operators are not linear, there is no linear relation, such as Eq. (146), between the Fourier images of the generalized force and generalized coordinate, and as the result there is no simple relation, such as Eq. (148), between their spectral densities. In other words, if the Heisenberg equation of motion are nonlinear, there is no regular simple way to use them to calculate statistical properties of the observables. For example, let us return to the dephasing problem described by Eqs. (68)-(70), and assume that the generalized force is characterized by relations similar to (93) and (134). Now writing the Heisenberg equations of motion for the two remaining spin operators, and using the commutation relations between them, we get

$$\dot{\hat{\sigma}}_x = -2 \frac{a - \hat{f}(t)}{\hbar} \hat{\sigma}_y, \quad \dot{\hat{\sigma}}_y = 2 \frac{a - \hat{f}(t)}{\hbar} \hat{\sigma}_x. \quad (7.156)$$

These equations do not provide a linear relation between the Pauli operators and the fluctuation force, so even if we know spectral properties of the latter from the FDT, this does not help too much - unless we return to the approximate, classical approach described in Sec. 3 above.⁵⁹

⁵⁸ Its natural generalizations enable analyses of fluctuations in arbitrary linear systems, i.e. the systems described by linear differential (or integro-differential) equations of motion, including those with many degrees of freedom, and distributed systems (*continua*).

⁵⁹ For some calculations, this problem may be avoided by *linearization*: if we are only interested in small fluctuations, the Heisenberg equations of motion may be linearized about their expectation values (see, e.g., CM Sec. 4.2), and the linear equations for variations solved either as has been shown above, or (if the expectation values evolve in time) by their Fourier expansions.

7.6. Density matrix approach

The main alternative approach, that is essentially a generalization of that used in Sec. 2, is to extract the final results from the dynamics of the density matrix of our subsystem s of interest (which, from this point on, will be called w_s). I will discuss this approach in detail,⁶⁰ cutting just a few technical corners, in each case referring the reader to special literature.

We already know that the density matrix allows the calculation of the expectation value of any observable of system s – see Eq. (5). However, our initial recipe (6) for the density matrix calculation, which requires the knowledge of the exact state (2) of the whole Universe, is not too practicable, while the von Neumann equation (66) for the density matrix evolution is limited to cases in which probabilities W_j of the system states are fixed – thus excluding such important effects as the energy relaxation. However, such effects may be analyzed using a different assumption – that the system of interest interacts only with some *local* environment (say, with the lab room) that is in the thermally-equilibrium state described by a diagonal density matrix – see Eqs. (15) and (23).

This calculation is facilitated by the following observation. Let us number the basis states of the full local system (the system of our interest plus its local environment) by index l , and apply Eq. (5) to write

$$\langle A \rangle = \text{Tr}(\hat{A}\hat{w}) = \sum_{l,l'} A_{ll'} w_{l'l} = \sum_{l,l'} \langle l | \hat{A} | l' \rangle \langle l' | \hat{w} | l \rangle, \quad (7.157)$$

where $\hat{w}$ is the statistical operator of this full composite system. At weak interaction between the system s and local environment e , their variables reside in different Hilbert spaces, so that we can write

$$|l\rangle = |s_j\rangle \otimes |e_k\rangle. \quad (7.158)$$

and if observable A depends only on the coordinates of system s , Eq. (157) yields

$$\begin{aligned} \langle A \rangle &= \sum_{\substack{j,j' \\ k,k'}} \langle e_k | \otimes \langle s_j | \hat{A} | s_{j'} \rangle \otimes | e_{k'} \rangle \langle e_{k'} | \otimes \langle s_{j'} | \hat{w} | s_j \rangle \otimes | e_k \rangle \\ &= \sum_{\substack{j,j' \\ k,k'}} \langle s_j | \hat{A} | s_{j'} \rangle \delta_{kk'} \langle e_{k'} | \otimes \langle s_{j'} | \hat{w} | s_j \rangle \otimes | e_k \rangle = \sum_{j,j'} A_{jj'} \langle s_{j'} | \left(\sum_k \otimes \langle e_k | \hat{w} | e_k \rangle \otimes \right) | s_j \rangle = \text{Tr}_j(\hat{A}\hat{w}_s), \end{aligned} \quad (7.159)$$

where $\hat{w}_s$ is defined as

$$\hat{w}_s \equiv \sum_k \langle e_k | \hat{w} | e_k \rangle = \text{Tr}_e \hat{w}. \quad (7.160)$$

Since Eq. (159) is similar to Eq. (5), $\hat{w}_s$ may serve as the statistical operator defined in the Hilbert space of the system of our interest. The huge advantage of Eqs. (159)-(160) is that they are valid for an *arbitrary* state of the local environment, including the case when it is in the thermodynamic equilibrium. By the way, the similarity of Eqs. (5) and (159) may serve as the strong argument, promised in Sec. 1, for the validity of the former relation even if the Universe as a whole is not in a pure state. (The argument is, however, imperfect, because the latter relation has been derived from the former one.)

⁶⁰ As in Sec. 4, the reader not interested in the derivation of the basic equation (181) for the density matrix evolution may immediately jump to the discussion of this equation and its applications.

Now, since at a sufficiently large size of the local environment e , the composite system $(s + e)$ may be considered Hamiltonian, with fixed probabilities of its states, for the description of time evolution of *its* statistical operator $\hat{w}$ (again, in contrast to that, $\hat{w}_s$, of the system of our interest) we may use the von Neumann equation (66). Partitioning its right-hand part in accordance with Eq. (68), we get:

$$i\hbar\dot{\hat{w}} = [\hat{H}_s, \hat{w}] + [\hat{H}_e, \hat{w}] + [\hat{H}_{\text{int}}, \hat{w}]. \quad (7.161)$$

The next step is to use the perturbation theory to solve this equation in the lowest order in $\hat{H}_{\text{int}}$ that yields nonvanishing results due to the interaction. For that, Eq. (161) is not very convenient, because its right-hand part contains two other terms, which are much larger than the interaction Hamiltonian. To mitigate this technical difficulty, the *interaction picture* (which was discussed in the end of Sec. 4.6), is very handy - though not absolutely necessary.

As a reminder, in that picture (whose entities will be marked with index I , with the unmarked operators assumed to be in the Schrödinger picture), both the operators *and* the state vectors (and hence the density matrix) depend on time. However, the time evolution of the operator of any observable A is described by Eq. (67) with the *unperturbed* part of the Hamiltonian only – see Eq. (4.214). In our current case (68), this means

$$i\hbar\dot{\hat{A}}_I = [\hat{A}_I, \hat{H}_0]. \quad (7.162)$$

where the unperturbed Hamiltonian consists of two independent parts:

$$\hat{H}_0 \equiv \hat{H}_s + \hat{H}_e. \quad (7.163)$$

On the other hand, the state vector evolution is governed by the interaction evolution operator $\hat{u}_I$ that obeys Eqs. (4.215). Since this equation, using the interaction-picture Hamiltonian (4.216),

$$\hat{H}_I \equiv \hat{u}_0^\dagger \hat{H}_{\text{int}} \hat{u}_0, \quad (7.164)$$

is absolutely similar to the ordinary Schrödinger equation using the full Hamiltonian, we may repeat all arguments given in the beginning of Sec. 3 to conclude that the dynamics of the density matrix in the interaction picture of a Hamiltonian system is governed by the following analog of the von Neumann equation (66):

$$i\hbar\dot{\hat{w}}_I = [\hat{H}_I, \hat{w}_I]. \quad (7.165)$$

Since this equation is similar in structure (with the opposite sign) to the Heisenberg equation (66), we may use solution Eq. (4.190) of the latter equation to write its analog:⁶¹

$$\hat{w}_I(t) = \hat{u}_I(t, 0) \hat{w}(0) \hat{u}_I^\dagger(t, 0). \quad (7.166)$$

It is also straightforward to verify that in this picture, the expectation value of any observable A may be found from the expression similar to the basic Eq. (5):

⁶¹ Notice the opposite order of the unitary operators, which results from the already mentioned sign difference. Note also that we could write a similar expression in the Schrödinger picture: $\hat{w}(t) = \hat{u} \hat{w}(0) \hat{u}^\dagger$, where $\hat{u}$ is the full time-evolution operator.

$$\langle A \rangle = \text{Tr}(\hat{A}_I \hat{w}_I), \quad (7.167)$$

so that the interaction and Schrödinger pictures give the same final results.

In the most frequent case of bilinear interaction (90),⁶² Eq. (162) is readily simplified, in different ways, for the both operators participating in the product. In particular, for $\hat{A} = \hat{x}$, it yields

$$i\hbar \dot{\hat{x}}_I = [\hat{x}_I, \hat{H}_0] = [\hat{x}_I, \hat{H}_s] + [\hat{x}_I, \hat{H}_e]. \quad (7.168)$$

Since operator of coordinate is defined in the Hilbert space of system s , it commutes with the Hamiltonian of the environment, so that we finally get

$$i\hbar \dot{\hat{x}}_I = [\hat{x}_I, \hat{H}_s]. \quad (7.169)$$

On the other hand, taking $\hat{A} = \hat{F}$, we should take into account that the last operator is defined in the Hilbert space of the environment, and commutes with the Hamiltonian of the unperturbed system s . As a result, we get

$$i\hbar \dot{\hat{F}}_I = [\hat{F}_I, \hat{H}_e]. \quad (7.170)$$

This means that with our time-independent unperturbed Hamiltonians $\hat{H}_s$ and $\hat{H}_e$, the time evolution of the interaction-picture operators is rather simple. In particular, the analogy between Eq. (170) and Eq. (93) allows us to immediately write the following analog of Eq. (94):

$$\hat{F}_I(t) = \exp\left\{\frac{i}{\hbar} \hat{H}_e t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t\right\}, \quad (7.171)$$

so that in the stationary (eigenstate) basis of the environment,

$$(\hat{F}_I)_{nm'}(t) = \exp\left\{\frac{i}{\hbar} E_n t\right\} F_{nm'}(0) \exp\left\{-\frac{i}{\hbar} E_{n'} t\right\} = F_{nm'}(0) \exp\left\{-i \frac{E_n - E_{n'}}{\hbar} t\right\}, \quad (7.172)$$

and similarly (but in the basis of the eigenstates of system s) for operator $\hat{x}$. As a result, Eq. (164) may be also factored:

$$\begin{aligned} \hat{H}_I(t) &\equiv \hat{u}_0^\dagger(t,0) \hat{H}_{\text{int}} \hat{u}_0(t,0) = \exp\left\{\frac{i}{\hbar} (\hat{H}_s + \hat{H}_e) t\right\} (-\hat{x} \hat{F}) \exp\left\{-\frac{i}{\hbar} (\hat{H}_s + \hat{H}_e) t\right\} \\ &= -\left(\exp\left\{\frac{i}{\hbar} \hat{H}_s t\right\} \hat{x} \exp\left\{-\frac{i}{\hbar} \hat{H}_s t\right\}\right) \left(\exp\left\{\frac{i}{\hbar} \hat{H}_e t\right\} \hat{F}(0) \exp\left\{-\frac{i}{\hbar} \hat{H}_e t\right\}\right) = -\hat{x}_I(t) \hat{F}_I(t). \end{aligned} \quad (7.173)$$

Now, as in Sec. 4, we may rewrite Eq. (165) in the integral form:

$$\hat{w}_I(t) = \frac{1}{i\hbar} \int_{-\infty}^t [\hat{H}_I(t'), \hat{w}_I(t')] dt'; \quad (7.174)$$

⁶² A similar analysis of a more general case, when the interaction with environment may be represented as a sum of products of the type (90), may be found in a monograph by K. Blum, *Density Matrix Theory and Applications*, 3rd ed., Springer, 2012.

plugging this result, for time t' , into the right-hand part of Eq. (174) again, we get

$$\dot{\hat{w}}_I(t) = -\frac{1}{\hbar^2} \int_{-\infty}^t [\hat{H}_I(t), [\hat{H}_I(t'), \hat{w}_I(t')]] dt' = -\frac{1}{\hbar^2} \int_{-\infty}^t [\hat{x}(t) \hat{F}(t), [\hat{x}(t') \hat{F}(t'), \hat{w}_I(t')]] dt', \quad (7.175)$$

where, for the notation brevity, from this point on I will strip operators $\hat{x}$ and $\hat{F}$ of their index I . (Their time dependence indicates the interaction picture clearly enough.)

So far, this equation is exact (and cannot be solved analytically), but this is the right time to notice that even if we take the density matrix in its right-hand part equal to its unperturbed value (corresponding to no interaction between system s and its thermally-equilibrium environment e),

$$\hat{w}_I(t') \rightarrow \hat{w}_s(t') \hat{w}_e, \quad \text{with } \langle e_n | \hat{w}_e | e_{n'} \rangle = W_n \delta_{nn'}, \quad (7.176)$$

where e_n are the stationary states of the environment and W_n are the Gibbs probabilities (23), Eq. (175) would still provide some nonvanishing time evolution of the density operator. This is exactly the first nonvanishing perturbation we have been looking for. Now using Eq. (160), we find the equation of evolution of the density operator of our system of interest:

$$\dot{\hat{w}}_s(t) = -\frac{1}{\hbar^2} \int_{-\infty}^t \text{Tr}_n [\hat{x}(t) \hat{F}(t), [\hat{x}(t') \hat{F}(t'), \hat{w}_s(t') \hat{w}_e]] dt', \quad (7.177)$$

where the trace is over the stationary states of the environment. In order to spell out the right-hand part of Eq. (177), note again that the coordinate and force operators commute with each other (but not with themselves at different time moments!) and hence may be swapped, so that we may write

$$\begin{aligned} \text{Tr}_n [\dots, [\dots, \dots]] &= \hat{x}(t) \hat{x}(t') \hat{w}_s(t') \text{Tr}_n [\hat{F}(t) \hat{F}(t') \hat{w}_e] - \hat{x}(t) \hat{w}_s(t') \hat{x}(t') \text{Tr}_n [\hat{F}(t) \hat{w}_e \hat{F}(t')] \\ &\quad - \hat{x}(t') \hat{w}_s(t') \hat{x}(t) \text{Tr}_n [\hat{F}(t') \hat{w}_e \hat{F}(t)] + \hat{w}_s(t') \hat{x}(t') \hat{x}(t) \text{Tr}_n [\hat{w}_e \hat{F}(t') \hat{F}(t)] \\ &= \hat{x}(t) \hat{x}(t') \hat{w}_s(t') \sum_{n,n'} F_{nn'}(t) F_{n'n}(t') W_n - \hat{x}(t) \hat{w}_s(t') \hat{x}(t') \sum_{n,n'} F_{nn'}(t) W_n F_{n'n}(t') \\ &\quad - \hat{x}(t') \hat{w}_s(t') \hat{x}(t) \sum_{n,n'} F_{nn'}(t') W_n F_{n'n}(t) + \hat{w}_s(t') \hat{x}(t') \hat{x}(t) \sum_{n,n'} W_n F_{nn'}(t') F_{n'n}(t). \end{aligned} \quad (7.178)$$

Since the summation on both indices n and n' in this expression is over the same energy level set (of all eigenstates of the environment), we may swap the indices in any of the sums. Doing that in the terms with factors W_n , we turn them into $W_{n'}$, so that this factor becomes common:

$$\begin{aligned} \text{Tr}_n [\dots, [\dots, \dots]] &= \sum_{n,n'} W_n [\hat{x}(t) \hat{x}(t') \hat{w}_s(t') F_{nn'}(t) F_{n'n}(t') - \hat{x}(t) \hat{w}_s(t') \hat{x}(t') F_{n'n}(t) F_{nn'}(t') \\ &\quad - \hat{x}(t') \hat{w}_s(t') \hat{x}(t) F_{n'n}(t') F_{nn'}(t) + \hat{w}_s(t') \hat{x}(t') \hat{x}(t) F_{nn'}(t') F_{n'n}(t)]. \end{aligned} \quad (7.179)$$

Now using Eq. (172), we get

$$\begin{aligned}
\text{Tr}_n[\dots, [\dots, \dots]] &= \sum_{n, n'} W_n |F_{nn'}|^2 \left[\hat{x}(t) \hat{x}(t') \hat{w}_s(t') \exp\left\{i \frac{\tilde{E}(t-t')}{\hbar}\right\} - \hat{x}(t) \hat{w}_s(t') \hat{x}(t') \exp\left\{-i \frac{\tilde{E}(t-t')}{\hbar}\right\} \right. \\
&\quad \left. - \hat{x}(t') \hat{w}_s(t) \hat{x}(t) \exp\left\{i \frac{\tilde{E}(t-t')}{\hbar}\right\} + \hat{w}_s(t') \hat{x}(t) \hat{x}(t) \exp\left\{-i \frac{\tilde{E}(t-t')}{\hbar}\right\} \right] \quad (7.180) \\
&= \sum_{n, n'} W_n |F_{nn'}|^2 \cos \frac{\tilde{E}(t-t')}{\hbar} [\hat{x}(t), [\hat{x}(t'), \hat{w}_s(t')]] + i \sum_{n, n'} W_n |F_{nn'}|^2 \sin \frac{\tilde{E}(t-t')}{\hbar} [\hat{x}(t), \{\hat{x}(t'), \hat{w}_s(t')\}],
\end{aligned}$$

where $\{\dots, \dots\}$ means the anticommutator – see Eq. (4.34). Comparing the two double sums participating in this expression with Eqs. (108) and (111), we see that they are nothing else than, respectively, the symmetrized correlation function and the Green's function (multiplied by $\hbar/2$) of the time-difference argument $\tau = t - t' \geq 0$. As the result, Eq. (177) takes a very simple form:

$$\dot{\hat{w}}_s(t) = -\frac{1}{\hbar^2} \int_{-\infty}^t K_F(t-t') [\hat{x}(t), [\hat{x}(t'), \hat{w}_s(t')]] dt' - \frac{i}{2\hbar} \int_{-\infty}^t G(t-t') [\hat{x}(t), \{\hat{x}(t'), \hat{w}_s(t')\}] dt'. \quad (7.181)$$

Density
matrix'
time
evolution

Let me hope that the reader enjoys this beautiful result as much as I do, and that it is a sufficient intellectual award for his or her effort of following its derivation. It gives a self-sufficient equation for time evolution of the density matrix of the system of our interest (s), with the effects of its environment represented only by two real algebraic functions of τ – one (K_F) describing environment's fluctuations and another one (G) representing its the average response to system's dynamics. And most spectacularly, these are exactly the same functions as participate in the Heisenberg-Langevin approach to the problem, and hence related to each other by the fluctuation-dissipation theorem (134).

After a short celebration, let us acknowledge that Eq. (181) is still an integro-differential equation that needs to be solved together with Eq. (169). Such equations do not allow explicit analytical solutions except for very simple (and not very interesting) cases. For most applications, further simplifications should be made. One of them is based on the fact (which was already discussed in Sec. 3) that both environmental functions participating in Eq. (181) tend to zero when their argument τ becomes larger than certain environment correlation time τ_c , which is frequently much shorter than the time scales $T_{nn'}$ of the evolution of the density matrix elements. Moreover, the characteristic time scale of the coordinate operator evolution may be also short on the scale of $T_{nn'}$. In this limit, all arguments t' of the density operator giving substantial contributions to the right-hand part of Eq. (172) are so close to t that it does not matter whether its argument is t' or just t . This simplification ($t' \rightarrow t$) is known as the *Markov approximation*.⁶³ However, this approximation alone is still insufficient for finding the general solution of Eq. (181). Substantial further progress is possible in two important cases.

The most important of them is when the intrinsic Hamiltonian $\hat{H}_s$ of our system of interest is time-independent and has a very *discrete* eigenenergy spectrum E_n ,⁶⁴ with well-separated levels:

⁶³ Named after A. Markov (1856-1922; in older literature, “Markoff”), because the result of this approximation is a particular case of the *Markov process* whose future development is completely determined by its present state.

⁶⁴ Rather reluctantly, I will use this standard notation, E_n , for the eigenenergies of our system of interest (s), in hope that the reader would not confuse these discrete energy levels with the quasi-continuous energy levels of its environment, participating in particular in Eqs. (108) and (111). As a reminder, by this stage of our calculations the environment levels have disappeared, leaving behind their “trace functions” $K_F(\tau)$ and $G(\tau)$.

$$|E_n - E_{n'}| \gg \frac{\hbar}{T_{nn'}}. \quad (7.182)$$

Let us see what does this condition yield for Eq. (181) rewritten for the matrix elements in the stationary state basis (from this point on, I will drop index s for brevity):

$$\dot{w}_{nn'} = -\frac{1}{\hbar^2} \int_{-\infty}^t K_F(t-t') [\hat{x}(t), [\hat{x}(t'), \hat{w}]]_{nn'} dt' - \frac{i}{2\hbar} \int_{-\infty}^t G(t-t') [\hat{x}(t), \{\hat{x}(t'), \hat{w}\}]_{nn'} dt'; \quad (7.183)$$

after spelling out the commutators, it includes 4 operator products, which differ “only” by the operator order. Let us have a good look at the first product,

$$(\hat{x}(t)\hat{x}(t')\hat{w})_{nn'} = \sum_{m,m'} x_{nm}(t)x_{mm'}(t')w_{m'n'}, \quad (7.184)$$

where indices m and m' run over the same set of eigenenergies of the system s of our interest as indices n and n' . According to Eq. (169) with a time-independent H_s , matrix elements x_{nm} (in the stationary state basis) oscillate in time as $\exp\{i\omega_{nm}t\}$, so that

$$(\hat{x}(t)\hat{x}(t')\hat{w})_{nn'} = \sum_{m,m'} x_{nm}x_{mm'} \exp\{i(\omega_{nm}t + \omega_{mm'}t')\}w_{m'n'}, \quad (7.185)$$

where the coordinate matrix elements are in the Schrödinger picture now, and I have used the natural notation (6.85) for the quantum transition frequencies:

$$\hbar\omega_{nn'} \equiv E_n - E_{n'}. \quad (7.186)$$

According to condition (182), frequencies $\omega_{nn'}$ with $n \neq n'$ are much higher than the speed of evolution of the density matrix elements (in the interaction picture!) – in both the left-hand and right-hand parts of Eq. (183). As we already know from Sec. 6.5, this means that in the right-hand part of Eq. (183) we may keep only the terms that do not oscillate with frequencies $\omega_{nn'}$, because they would give negligible contribution to the density matrix dynamics.⁶⁵ For that, in the double sum (185) we may keep only the terms proportional to difference $(t - t')$, because they will give (after integration over t') a slowly changing contribution to the right-hand part.⁶⁶ These terms should have $\omega_{nm} + \omega_{mm'} = 0$, i.e. $(E_n - E_m) + (E_m - E_{m'}) \equiv E_n - E_{m'} = 0$. For a non-degenerate energy spectrum, this requirement means $m' = n$; as a result, the double sum is reduced to a single one:

$$(\hat{x}(t)\hat{x}(t')\hat{w})_{nn'} \approx \sum_m x_{nm}x_{mn} \exp\{i\omega_{nm}(t-t')\}w_{nn'} = \sum_m |x_{nm}|^2 \exp\{i\omega_{nm}(t-t')\}w_{nn'}. \quad (7.187)$$

Another product, $(\hat{w}\hat{x}(t')\hat{x}(t))_{nn'}$, that appears in the right-hand part of Eq. (183), may be simplified absolutely similarly, giving

$$(\hat{w}\hat{x}(t')\hat{x}(t))_{nn'} \approx \sum_m |x_{n'm}|^2 \exp\{i\omega_{n'm}(t'-t)\}w_{nn'}. \quad (7.188)$$

⁶⁵ This is essentially the same rotating-wave approximation (RWA) that is so instrumental in other fields of not only quantum mechanics, but classical physics as well – see, e.g., CM Secs. 4.2-4.5.

⁶⁶ As was already discussed in Sec. 4, the lower-limit substitution $(t' = -\infty)$ in integrals (174) gives zero, due to the finite-time “memory” of the system, expressed by the decay of the correlation and response functions at large values of the time delay $\tau = t - t'$.

These expressions hold true whether n and n' are equal or not. The situation is different for two other products in the right-hand part of Eq. (183), with w sandwiched between x and x' . For example,

$$(\hat{x}(t)\hat{w}\hat{x}(t'))_{nn'} = \sum_{m,m'} x_{nm}(t) w_{mm'} x_{m'n'}(t') = \sum_{m,m'} x_{nm} w_{mm'} x_{m'n'} \exp\{i(\omega_{nm}t + \omega_{m'n'}t')\}. \quad (7.189)$$

For this term, the same requirement of having a fast oscillating function of $(t - t')$ only yields a different condition: $\omega_{nm} + \omega_{m'n'} = 0$, i.e.

$$(E_n - E_m) + (E_{m'} - E_{n'}) = 0. \quad (7.190)$$

Here the double sum reduction is possible only if we make an additional assumption that all interlevel energy distances are unique, i.e. our system of interest has no equidistant levels (such as in the harmonic oscillator). For diagonal elements ($n = n'$), the RWA requirement is reduced to $m = m'$, giving sums over all diagonal elements of the density matrix:

$$(\hat{x}(t)\hat{w}\hat{x}(t'))_{nn} = \sum_m |x_{nm}|^2 \exp\{i\omega_{nm}(t - t')\} w_{nn}. \quad (7.191)$$

(Another similar term $(\hat{x}(t')\hat{w}\hat{x}(t))_{nn}$, is just a complex conjugate of Eq. (191).) However, for off-diagonal matrix elements ($n \neq n'$), the situation is different: Eq. (190) may be satisfied only if $m = n$ and also $m' = n'$, so that the double sum is reduced to just one, non-oscillating term:

$$(\hat{x}(t)\hat{w}\hat{x}(t'))_{nn'} = x_{nn} w_{nn'} x_{n'n'}, \quad \text{for } n \neq n'. \quad (7.192)$$

The second similar term, $(\hat{x}(t')\hat{w}\hat{x}(t))_{nn}$, is exactly the same, so that in one of the integrals of Eq. (183), these terms add up, while in the second one, they cancel.

This is why the final equations of evolution look differently for diagonal and off-diagonal elements of the density matrix. For the former case ($n = n'$), Eq. (183) is reduced to the so-called *master equation*⁶⁷ relating diagonal elements w_{nn} of the density matrix, i.e. the energy level occupancies W_n :⁶⁸

$$\dot{W}_n = \sum_{m \neq n} |x_{nm}|^2 \int_0^\infty \left[-\frac{1}{\hbar^2} K_F(\tau) (W_n - W_m) (\exp\{i\omega_{nm}\tau\} + \exp\{-i\omega_{nm}\tau\}) - \frac{i}{2\hbar} G(\tau) (-W_n - W_m) (\exp\{i\omega_{nm}\tau\} - \exp\{-i\omega_{nm}\tau\}) \right] d\tau, \quad (7.193)$$

where $\tau \equiv t - t'$. Changing the summation index notation from m to n' , we may rewrite the master equation in its canonical form

$$\dot{W}_n = \sum_{n' \neq n} (\Gamma_{n' \rightarrow n} W_{n'} - \Gamma_{n \rightarrow n'} W_n), \quad (7.194)$$

where coefficients

$$\Gamma_{n' \rightarrow n} \equiv |x_{nn'}|^2 \int_0^\infty \left[\frac{2}{\hbar^2} K_F(\tau) \cos \omega_{nn'} \tau - \frac{1}{\hbar} G(\tau) \sin \omega_{nn'} \tau \right] dt', \quad (7.195)$$

Master equations and interlevel transition rates

⁶⁷ The master equations, first introduced to quantum mechanics in 1928 by W. Pauli, are sometimes called the “Pauli master equations”, or “kinetic equations”, or “rate equations”.

⁶⁸ As Eq. (193) shows, the term with $m = n$ would vanish, and thus may be legitimately excluded from the sum.

are called the *interlevel transition rates*.⁶⁹ Equation (194) has a very clear physical meaning of the level occupancy dynamics (i.e. the balance of probability flows ΓW) due to the quantum transitions between the energy levels (Fig. 6), in our current case caused by the interaction between the system of our interest and its environment.⁷⁰

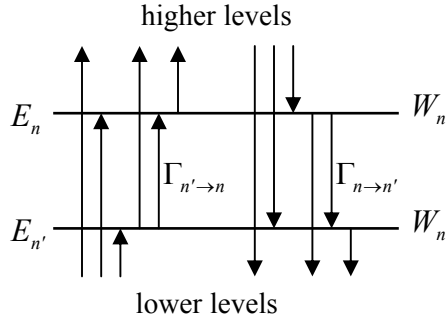


Fig. 7.6. Probability flows between the energy levels, described by the master equation (186).

The Fourier transforms (113) and (123) enable us to express two integrals in Eq. (195) via, respectively, the symmetrized spectral density $S_F(\omega)$ of environment force fluctuations and the imaginary part $\chi''(\omega)$ of the generalized susceptibility, both at frequency $\omega = \omega_{nn'}$. After that we may use the fluctuation-dissipation theorem (134) to exclude the former function, getting finally

$$\Gamma_{n' \rightarrow n} = \frac{1}{\hbar} |x_{nn'}|^2 \chi''(\omega_{nn'}) \left(\coth \frac{\hbar \omega_{nn'}}{2k_B T} - 1 \right) = \frac{2}{\hbar} |x_{nn'}|^2 \frac{\chi''(\omega_{nn'})}{\exp\{(E_n - E_{n'})/k_B T\} - 1}. \quad (7.196)$$

Note that since the imaginary part of the generalized susceptibility is an odd function of frequency, Eq. (196) is in compliance with the Gibbs distribution for arbitrary temperature. Indeed, according to this equation, the ratio of “up” and “down” rates for each pair of levels equals

$$\frac{\Gamma_{n' \rightarrow n}}{\Gamma_{n \rightarrow n'}} = \frac{\chi(\omega_{nn'})}{\exp\{(E_n - E_{n'})/k_B T\} - 1} / \frac{\chi(\omega_{n'n})}{\exp\{(E_{n'} - E_n)/k_B T\} - 1} = \exp\left\{-\frac{E_n - E_{n'}}{k_B T}\right\}. \quad (7.197)$$

On the other hand, according to the Gibbs distribution (23), in thermal equilibrium the level populations should be in the same proportion, satisfying the so-called *detailed balance equations*,

$$W_n \Gamma_{n \rightarrow n'} = W_{n'} \Gamma_{n' \rightarrow n}, \quad (7.198)$$

for each pair $\{n, n'\}$, so that all right-hand parts of all Eqs. (194) could vanish – as they should. Thus, the stationary solution of the master equations indeed describes the thermal equilibrium.

The closed system of master equations (194), sometimes complemented by additional right-hand-part terms that describe interlevel transitions due to other factors (e.g., by an external ac force with a frequency close to one of $\omega_{nn'}$), is the key starting point for practical analyses of many quantum

⁶⁹ As Eq. (193) shows, the result for $\Gamma_{n \rightarrow n'}$ is described by Eq. (195) as well, provided that indices n and n' are swapped in all components of its right-hand part, including the swap $\omega_{nn'} \rightarrow \omega_{n'n} = -\omega_{nn'}$.

⁷⁰ It is straightforward to show that at relatively low temperatures ($k_B T \ll |E_{n'} - E_n|$), Eq. (196) gives the same result as the Golden Rule formula (6.134) – see Exercise 2. (The low temperature limit is necessary to ensure that the initial occupancy of the excited level is negligible, as was assumed at the derivation of Eq. (6.134).)

systems including quantum generators (masers and lasers). It is important to remember that it is strictly valid only in the rotating-wave approximation, i.e. if Eq. (182) is well satisfied for all n and n' .

For a particular (but very important) case of a two-level system (say, with $E_1 > E_2$) in the low-temperature limit $k_B T \ll \hbar \omega_{12} = E_1 - E_2$, rate $\Gamma_{1 \rightarrow 2} \gg \Gamma_{2 \rightarrow 1}$ defines the characteristic time $T_1 \equiv 1/\Gamma_{1 \rightarrow 2}$ of the *energy relaxation* process that brings the *diagonal* elements of the density matrix to their thermally-equilibrium values (23). For the Ohmic dissipation described by Eq. (138), Eq. (196) yields a simple expression

$$\frac{1}{T_1} \equiv \Gamma_{1 \rightarrow 2} = \frac{2k_B T}{\hbar^2} |x_{12}|^2 \eta. \quad (7.199)$$

Energy
relaxation
time

Of course, time T_1 should not be confused with the characteristic time T_2 of relaxation of the *off-diagonal* elements, i.e. dephasing, which was already discussed in Sec. 3. By the way, let us see what do Eqs. (183) say about the dephasing rate. Taking into account our intermediate results (187)-(192), and merging the non-oscillating components (with $m = n$ and $m = n'$) of sums Eq. (187) and (188) with the terms (192), that also do not oscillate in time, we get the following equation:⁷¹

$$\dot{w}_{nn'} = - \left\{ \int_0^\infty \left[\frac{1}{\hbar^2} K_F(\tau) \left(\sum_{m \neq n} |x_{nm}|^2 \exp\{i\omega_{nm}\tau\} + \sum_{m \neq n'} |x_{n'm}|^2 \exp\{-i\omega_{n'm}\tau\} + (x_{nn} - x_{n'n'})^2 \right) + \frac{i}{2\hbar} G(\tau) \left(\sum_{m \neq n} |x_{nm}|^2 \exp\{i\omega_{nm}\tau\} - \sum_{m \neq n'} |x_{n'm}|^2 \exp\{-i\omega_{n'm}\tau\} \right) \right] d\tau \right\} w_{nn'}, \text{ for } n \neq n'. \quad (7.200)$$

In contrast with Eq. (194), the right-hand part of this equation includes both a real and an imaginary part, and hence it may be presented as

$$\dot{w}_{nn'} = -(1/T_{nn'} + i\Delta_{nn'}) w_{nn'}, \quad (7.201)$$

where both factors $1/T_{nn'}$ and $\Delta_{nn'}$ are real.⁷² As should be clear from Eq. (201), the second term in the right-hand part of this equation causes slow oscillations of the matrix elements $w_{nn'}$; that, after returning to the Schrödinger picture, add just small corrections⁷³ to the unperturbed frequencies (183) of their oscillations, and are hence are not important for most applications. More important is the first term,

⁷¹ Because of the reason explained above, this (relatively :-) simple result is not valid for systems with equidistant energy spectra, most importantly, for the harmonic oscillator (while Eq. (7.194) is). For the oscillator, with its simple matrix elements $x_{nn'}$, it is straightforward to repeat the above calculations, starting from (7.183), to obtain an equation similar to Eq. (7.200), but with two other terms, proportional to $w_{n \pm 1, n' \pm 1}$, in its right-hand part. Since for the harmonic oscillator the Heisenberg-Langevin approach allows obtaining most results in a much simpler way, I will skip the derivation of this equation and the discussion of its solutions. The interested reader may find such a discussion, for example, in a paper by B. Zeldovich *et al.*, *Sov. Phys. JETP* **28**, 308 (1969).

⁷² Sometimes Eq. (200) (in any of its numerous alternative forms) is called the *Redfield equation*, after the 1965 work by A. Redfield. Note, however, that several other authors, notably including (in the alphabetical order) H. Haken, W. Lamb, M. Lax, W. Louisell, and M. Scully, also made key contributions into the very fast development of the density-matrix approach to open quantum systems in the mid-1960s.

⁷³ This correction is frequently called the *Lamb shift*, because it was first observed experimentally in 1947 by W. Lamb and R. Retherford, as a minor, ~ 1 GHz shift between energy levels of $2s$ and $2p$ states of hydrogen, due to the electric-dipole coupling of hydrogen atoms to the free-space electromagnetic environment. (These levels are equal not only in the nonrelativistic theory (Sec. 3.6), but also in the relativistic, Dirac theory (Sec. 9.7), if the

$$\frac{1}{T_{nn'}} = \int_0^\infty \left[\frac{1}{\hbar^2} K_F(\tau) \left(\sum_{m \neq n} |x_{nm}|^2 \cos \omega_{nm} \tau + \sum_{m \neq n'} |x_{n'm}|^2 \cos \omega_{n'm} \tau + (x_{nn} - x_{n'n'})^2 \right) - \frac{1}{2\hbar} G(\tau) \left(\sum_{m \neq n} |x_{nm}|^2 \sin \omega_{nm} \tau + \sum_{m \neq n'} |x_{n'm}|^2 \sin \omega_{n'm} \tau \right) \right] d\tau, \quad \text{for } n \neq n', \quad (7.202)$$

because it describes the effect absent without the environment: an exponential decay of the off-diagonal matrix elements, i.e. dephasing. Comparing the first 2 terms of Eq. (202) with Eq. (195), we see that the dephasing rates may be described by a very simple formula:

General
result
for
dephasing
rates

$$\begin{aligned} \frac{1}{T_{nn'}} &= \frac{1}{2} \left(\sum_{m \neq n} \Gamma_{n \rightarrow m} + \sum_{m \neq n'} \Gamma_{n' \rightarrow m} \right) + \frac{\pi}{\hbar^2} (x_{nn} - x_{n'n'})^2 S_F(0) \\ &= \frac{1}{2} \left(\sum_{m \neq n} \Gamma_{n \rightarrow m} + \sum_{m \neq n'} \Gamma_{n' \rightarrow m} \right) + \frac{k_B T}{\hbar^2} \eta (x_{nn} - x_{n'n'})^2, \quad \text{for } n \neq n', \end{aligned} \quad (7.203)$$

where the low-frequency viscosity coefficient η is again defined as $\lim_{\omega \rightarrow 0} \chi''(\omega)/\omega$ - see Eq. (138).

This result shows that two effects yield independent contributions into dephasing. The first of them may be interpreted as a result of the “virtual” transitions of the system to other energy levels m ; according to Eq. (187), it is proportional to the strength of coupling to environment at relatively high frequencies ω_{nm} and $\omega_{n'm}$. (If the energy quanta $\hbar\omega$ of these frequencies are much larger than the thermal fluctuation scale $k_B T$, only the lower levels, with $E_m < \max[E_n, E_{n'}]$ are important.) On the contrary, the second contribution is due to low-frequency, essentially classical fluctuations of the environment, and hence to the low-frequency dissipative susceptibility. If the susceptibility (more exactly, the ratio $\eta = \chi''(\omega)/\omega$) is frequency-independent, both contributions are of the same order, but their exact relation depends on the relation between the matrix elements $x_{nn'}$ of a particular system.

Returning again to the two-level system discussed in Sec. 3, the high-frequency contributions vanish because of the absence of transitions between its energy levels, while the low-frequency contribution yields

$$\frac{1}{T_2} \equiv \frac{1}{T_{12}} = \frac{k_B T}{\hbar^2} \eta (x_{11} - x_{22})^2 \rightarrow \frac{k_B T}{\hbar^2} \eta [(\sigma_z)_{11} - (\sigma_z)_{22}]^2 = \frac{4k_B T}{\hbar^2} \eta, \quad (7.204)$$

thus exactly reproducing the result (142) of the Heisenberg-Langevin approach.⁷⁴ Note also that Eq. (204) for T_2 is very close in structure to Eq. (199) for T_1 . For our simple interaction model (70), the off-diagonal elements of operator $\hat{x} = \hat{\sigma}_x$ in the stationary-state z -basis vanish, so that $T_1 \rightarrow \infty$. For the two-well implementation of the model (see Fig. 4 and its discussion), this result corresponds to a very high energy barrier between the wells, that inhibits tunneling, and hence any change of well occupancies W_L

electromagnetic environment is ignored.) The explanation of the shift, by H. Bethe in the same 1947, has launched the whole field of quantum electrodynamics – to be briefly discussed in Chapter 9.

⁷⁴ The first form of Eq. (203), as well as the analysis of Sec. 3, imply that low-frequency fluctuations of any other origin, not taken into account in own current calculations (say, unintentional noise from experimental equipment), may also cause dephasing; such “technical fluctuations” are indeed a serious challenge at the experimental implementation of coherent qubit systems – see Sec. 8.5 below.

and W_R . However, T_1 may become finite, and comparable with T_2 , if tunneling between the wells is substantial.⁷⁵

Now let us briefly discuss dissipative systems with *continuous* spectrum. Unfortunately, for them the only (relatively :-) simple results that may be obtained from Eq. (181) are essentially classical in nature. As an illustration, let us consider the simplest example of a 1D particle that interacts with a thermally-equilibrium environment, but otherwise is free to move (unconfined). As we know from Chapters 2 and 5, in this case the most convenient basis is that of momentum eigenstates p . In the momentum representation, the density matrix is just the c -number function $w(p, p')$, defined by Eq. (54), that has already been discussed in brief in Sec. 2. On the other hand, the coordinate operator, that also participates in the right-hand part of Eq. (181), has the form given by the first of Eqs. (5.64),

$$\hat{x} = i\hbar \frac{\partial}{\partial p}, \quad (7.205)$$

dual to the coordinate representation formula (5.29). As we already know, such operators are local – see, e.g., Eq. (5.28b). Due to this locality, the whole right-hand part of Eq. (181) is local as well, and hence (within the framework of our perturbative treatment) the interaction with environment affects essentially only the diagonal values $w(p, p)$ of the density matrix, i.e. the momentum probability density $w(p)$. Let us find the equation governing the evolution of this function in time.

Generally, in the interaction picture, matrix elements of operators $\hat{x}$ and $\hat{w}$ acquire some time dependence, but in the limit $p' \rightarrow p$, this dynamics lacks the high frequencies (186) that have been so helpful for the derivation of master equations. As a result, the only serious simplification of Eq. (181) is possible in the Markov approximation, when the time scale of the density matrix evolution is much longer than the correlation time τ_c of the environment, i.e. the time scale of functions $K_F(\tau)$ and $G(\tau)$. In this approximation, we may take the matrix elements out of the first integral of Eq. (181),

$$\begin{aligned} -\frac{1}{\hbar^2} \int_{-\infty}^t K_F(t-t') dt' [\hat{x}(t), [\hat{x}(t'), \hat{w}(t')]] &\approx -\frac{1}{\hbar^2} \int_0^\infty K_F(\tau) d\tau [\hat{x}, [\hat{x}, \hat{w}]] \\ &= -\frac{\pi}{\hbar^2} S_F(0) [\hat{x}, [\hat{x}, \hat{w}]] = -\frac{k_B T}{\hbar^2} \eta [\hat{x}, [\hat{x}, \hat{w}]], \end{aligned} \quad (7.206)$$

and calculate the double commutator in the Schrödinger picture. This may be done either using an explicit expression for the matrix elements of the coordinate operator, dual to Eq. (5.28b), or in a simpler way, using the same trick as at the derivation of the Ehrenfest theorem in Sec. 5.2. Namely, expanding an arbitrary function $f(p)$ into the Taylor series in one of its arguments (say, p),

$$f(p) = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k f}{\partial p^k} p^k, \quad (7.207)$$

and applying Eq. (205) to each term, we can prove the following simple commutation relation:

⁷⁵ The tunneling may be described without altering Eq. (70), just by adding, to the unperturbed Hamiltonian (69), terms proportional to other Pauli matrices. The reader is encouraged to spell out the equations for the time evolution of the density matrix elements of this system, and analyze their main properties – at least in the low-temperature limit.

$$[\hat{x}, f] = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k f}{\partial p^k} [\hat{x}, p^k] = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k f}{\partial p^k} (i\hbar k p^{k-1}) = i\hbar \sum_{k=1}^{\infty} \frac{1}{(k-1)!} \frac{\partial^{k-1}}{\partial p^{k-1}} \left(\frac{\partial f}{\partial p} \right) p^{k-1} = i\hbar \frac{\partial f}{\partial p}. \quad (7.208)$$

Now applying this result sequentially, first to $w(p, p')$ and then to the resulting commutator, we get

$$[\hat{x}, [\hat{x}, w]] = \left[\hat{x}, i\hbar \frac{\partial w}{\partial p} \right] = i\hbar \frac{\partial}{\partial p} \left(i\hbar \frac{\partial w}{\partial p} \right) = -\hbar^2 \frac{\partial^2 w}{\partial p^2}. \quad (7.209)$$

It may look like the second integral in Eq. (181) might be simplified similarly. However, it vanishes at $p' \rightarrow p$, and $t' \rightarrow t$, so that in order to calculate the first nonvanishing contribution from that integral for $p = p'$, we have to take into account the small difference $\tau \equiv t - t' \sim \tau_c$ between the arguments of the coordinate operators under that integral. This may be done using Eq. (169) with the free-particle Hamiltonian consisting of the kinetic-energy contribution alone:

$$\hat{x}(t') - \hat{x}(t) \approx -\tau \dot{\hat{x}} = -\tau \frac{1}{i\hbar} [\hat{x}, \hat{H}_s] = -\tau \frac{1}{i\hbar} \left[\hat{x}, \frac{\hat{p}^2}{2m} \right] = -\tau \frac{\hat{p}}{m}, \quad (7.210)$$

where the exact argument of the operator in the right-hand part is already unimportant, and may be taken for t . As a result, we may use the last of Eqs. (136) to reduce the second term in the right-hand part of Eq. (181) to

$$-\frac{i}{2\hbar} \int_{-\infty}^t G(t-t') [\hat{x}(t), \{\hat{x}(t'), \hat{w}(t')\}] dt' \approx \frac{i}{2\hbar} \int_0^{\infty} G(\tau) \tau d\tau \left[\hat{x}, \left\{ \frac{\hat{p}}{m}, \hat{w} \right\} \right] = \frac{\eta}{2i\hbar} \left[\hat{x}, \left\{ \frac{\hat{p}}{m}, \hat{w} \right\} \right]. \quad (7.211)$$

In the momentum representation, the momentum operator and the density matrix w are just c -numbers and commute, so that, applying Eq. (208) to product pw , we get

$$\left[\hat{x}, \left\{ \frac{\hat{p}}{m}, \hat{w} \right\} \right] = \left[\hat{x}, 2 \frac{p}{m} w \right] = 2i\hbar \frac{\partial}{\partial p} \left(\frac{p}{m} w \right), \quad (7.212)$$

and may finally reduce the integro-differential equation Eq. (181) to a partial differential equation:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial p} \left(\eta \frac{p}{m} w \right) + k_B T \eta \frac{\partial^2 w}{\partial p^2}. \quad (7.213)$$

This is the 1D form of the famous *Fokker-Planck equation* describing the classical statistics of motion of a free 1D particle in a medium with linear viscosity η . The first, *drift* term in the right-hand part of Eq. (213) describes particle's deceleration due to the average viscous force (137), $\langle F \rangle = -\eta v = -\eta p/m$, provided by the environment, while the second, *diffusion* term describes the effect of fluctuations: particle's random walk that obeys Eq. (85) with the diffusion coefficient

$$D = \eta k_B T. \quad (7.214)$$

This fundamental *Einstein relation*,⁷⁶ shows again the intimate connection between the dissipation (viscosity) and fluctuations, in this classical limit represented by their thermal energy scale $k_B T$.⁷⁷

⁷⁶ It was the main result of A. Einstein's pioneering analysis of such *Brownian motion* in 1905. (The development of this analysis in 1906-1908 by M. Smoluchowski has led in 1912 to the Fokker-Planck theory.)

Just for reader's reference, let me note that the Fokker-Planck equation (213) may be readily generalized to the 3D motion of a particle under the effect of an additional external force $F_{\text{ext}}(\mathbf{r}, t)$:⁷⁸

$$\frac{\partial w}{\partial t} = -\nabla \cdot \left(\frac{\mathbf{p}}{m} w \right) - \nabla_p \cdot (\mathbf{F} w) + D \nabla_p^2 w, \quad \text{with } \mathbf{F} = \mathbf{F}_{\text{ext}} - \eta \frac{\mathbf{p}}{m}, \quad (7.215)$$

3D
Fokker-
Planck
equation

where $w = w(\mathbf{r}, \mathbf{p}, t)$ is the time-dependent probability density in the 6D phase space, and ∇_p is the nabla/del operator of differentiation over the momentum components, defined similarly to its coordinate counterpart ∇ . The Fokker-Planck equation in this form is the basis for many important applications; however, due to its classical character, its discussion is left for the SM part of my lecture notes.⁷⁹

To summarize our discussion of the two alternative approaches to the analysis of quantum systems interacting with a thermally-equilibrium environment, described in the last three sections, let me emphasize that they give descriptions of the same phenomena, and are characterized by the same two functions $G(\tau)$ and $K_F(\tau)$, but from two different points of view. Namely, in the Heisenberg-Langevin approach we describe the system by operators that change (fluctuate) in time, even in thermal equilibrium, while in the density-matrix approach the system is described by non-fluctuating probability functions, such as $W_n(t)$ or $w(p)$, that are stationary in equilibrium. In the (relatively rare) cases when a problem may be solved by either method, they give identical results for all observables.

7.7. Quantum measurements

Now we have got a sufficient quantum mechanics background for a brief discussion of *quantum measurements*.⁸⁰ Let me start with reminding the reader the only postulate of quantum mechanics that relates this theory with experiment. In Chapter 4 it was formulated for a pure state described with ket-vector

$$|\alpha\rangle = \sum_j \alpha_j |a_j\rangle, \quad (7.216)$$

⁷⁷ This classical relation may be derived using several other ways – including those much simpler than used above. For example, since the Brownian particle's motion may be described by a linear Langevin equation, Eq. (214) may be readily obtained from the Nyquist formula (139) – see, e.g., SM Sec. 5.5.

⁷⁸ Moreover, Eq. (213) may be generalized to the motion in an additional periodic potential $U(\mathbf{r})$. In this case, an analog of Eq. (215) for the probability density of quasi-momentum $\hbar\mathbf{q}$ (rather than the genuine momentum $\mathbf{p}$) includes an additional energy band index (say, n), an additional force $\mathbf{F}_n = -\nabla E_n$ (where $E_n(\mathbf{q})$ is the energy band structure that was discussed in Secs. 2.7 and 3.4), and an additional term similar to the right-hand part of Eq. (194), describing interband transitions with quasi-momentum-dependent rates $\Gamma_{n \rightarrow m}(\mathbf{q})$. These rates are still expressed by Eq. (196), but with the matrix elements $x_{nn'}$ replaced by those of the vector operator $\hat{\Omega} \equiv \hat{\mathbf{r}} - i\nabla_q$ of interband transitions, which was discussed in Chapter 5. For details and a particular example of a sinusoidal potential see, e.g., K. Likharev and A. Zorin, *J. Low Temp. Phys.* **59**, 347 (1985).

⁷⁹ For a more detailed analysis and several examples of quantum effects in dissipative systems with continuous spectra see, e. g., U. Weiss, *Quantum Dissipative Systems*, 2nd ed., World Scientific, 1999, or H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems*, Oxford U. Press, 2007.

⁸⁰ “Quantum measurements” is a very unfortunate term; it would be more sensible to speak about “measurements of quantum mechanical observables”. However, the former term is so common and compact that I will use it.

where a_j and A_j are, respectively, the eigenstates of the operator of observable A , defined by Eq. (4.68). According to the postulate, the outcome of each particular measurement of observable A may be uncertain,⁸¹ but is restricted to the set of eigenstates A_j , with the probability of outcome A_j equal to

$$W_j = |\alpha_j|^2. \quad (7.217)$$

Since we know now that the state of the system (or rather of the statistical ensemble of similar systems we are using for measurements) is generally not pure, this postulate should be re-worded as follows: even if the system is in the *least uncertain* state (216), the measurement outcomes are still probabilistic, and obey Eq. (133).⁸²

Quantum measurement may be understood as a procedure of transferring the “microscopic” information contained in coefficients α_j into “macroscopically” available information about the outcomes of particular experiments, that may be recorded and reliably stored – say, on paper, or in a computer, or in our minds. If we believe that such transfer may be always done well enough, and do not worry too much how exactly, we are subscribing to the *mathematical* notion of measurement, that was (rather reluctantly) used in these notes – up to this point. However, every physicist should understand that measurements are performed by *physical devices* that also should obey the laws of quantum mechanics, and it is important to understand the basic laws of their operation.

The founding fathers of quantum mechanics have not paid much attention to these issues, probably because of the following two reasons. First, at that time it looked like the experimental instruments (at least the best of them :-)) were doing exactly what postulate (217) was telling. For example, had not the z -oriented Stern-Gerlach experiment turned two complex coefficients $\alpha_\uparrow$ and $\alpha_\downarrow$, describing the incoming electron beam, into particle counter clicks with rates proportional to, respectively, $|\alpha_\uparrow|^2$ and $|\alpha_\downarrow|^2$? Also, the crude internal nature of these instruments made more detailed questions unnatural. For example, the electron rate counting with a Geiger counter involves an effective disappearance of each incoming electron inside a zillion-particle electric discharge avalanche. Thinking about such devices, it was hard to even imagine measurements that would not disturb the quantum state of the particle being measured.

However, since that time the experimental techniques, notably including high vacuum, low temperatures, and low-noise electronics, have much improved, and eventually more inquisitive questions started to look not so hopeless. In my scheme of things, these questions may be grouped as follows:

(i) What are the main laws of a quantum measurement as a physical process? In particular, should it always involve time irreversibility? a human/intelligent observer? (The last question is not as laughable as it may look – see below.)

(ii) What is the state of the measured system just *after* a *single-shot* measurement - meaning the measurement process limited to a time interval much shorter than the time scale of measured system’s evolution? This question is naturally related to the issues of *repeated measurements* and *continuous monitoring* of system’s state.

⁸¹ Besides the trivial case $\alpha_j = \delta_{ij}$ (so that $W_j = \delta_{ij}$), when the system is in a certain eigenstate (a_j) of operator $\hat{A}$.

⁸² The reader in doubt is invited to compare *entropy* $\mathcal{S} = -\sum_j W_j \ln W_j$, the measure of system’s disorder (see, e.g., SM Sec. 2.2) of the pure state ($\mathcal{S} = 0$) with that in any state with several nonvanishing values of W_j ($\mathcal{S} > 0$).

(iii) If a measurement of observable A produced a certain outcome A_j , can we believe that the system had been in the corresponding state α_j just *before* the measurement?

The last question is most closely related to various interpretations of quantum mechanics, and will be discussed in the concluding Chapter 10, and now let me provide some input on the first two groups of issues.

First of all, I am happy to report that there is a virtual consensus of physicists on the two first questions of series (i). According to this consensus, any quantum measurement needs to result in a certain, distinguishable state of a macroscopic output component of the measurement instrument - see Fig. 7. (Traditionally, its component is called a *pointer*, though its role may be played by a printer or a plotter, an electronic circuit sending out the result as a number, etc.).

This requirement implies that the measurement process should have the following features:

- be time-irreversible ,
- provide large “signal gain”, i.e. mapping the quantum process with its $\hbar$ -scale of action (i.e. of the energy-by-time product) onto a macroscopic motion of the pointer with a much larger action scale, and
- if we want high measurement fidelity, the process should introduce as little additional uncertainty as permitted by the law of physics.

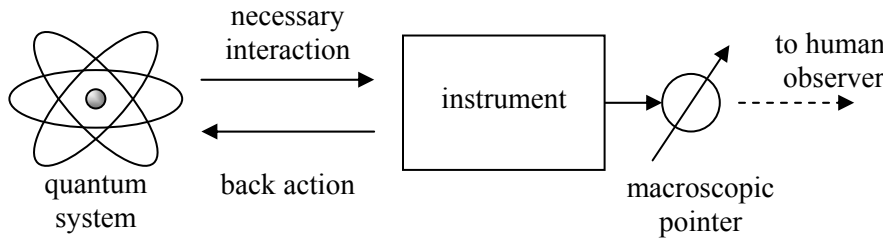


Fig.7.7. General scheme of quantum measurement.

All these requirements *are* fulfilled in a good Stern-Gerlach experiment. However, since the internal physics of the particle detector at this measurement is rather complex, let me give an example of a different, more simple single-shot scheme⁸³ capable of measuring the instant state of a typical two-level system, for example, a particle in a double quantum well potential (Fig. 8).⁸⁴ Let the system be, at $t = 0$, in a pure quantum state described by ket-vector

$$|\alpha\rangle = \alpha_{\rightarrow}|\rightarrow\rangle + \alpha_{\leftarrow}|\leftarrow\rangle, \quad (7.218)$$

⁸³ This scheme may be implemented, for example, using a simple Josephson-junction circuit called the *balanced comparator* - see, e.g., T. Walls *et al.*, *IEEE Trans. on Appl. Supercond.* **17**, 136 (2007), and references therein. Experiments by V. Semenov *et al.*, *IEEE Trans. Appl. Supercond.* **7**, 3617 (1997) have demonstrated that this system may have measurement accuracy dominated by quantum-mechanical uncertainty at relatively modest cooling (to ~ 1 K). One of advantages of such implementation of this measurement scheme is that it is based on externally-shunted Josephson junctions – devices whose quantum-mechanical model is in a quantitative agreement with experiment - see, e.g., D. Schwartz *et al.*, *Phys. Rev. Lett.* **55**, 1547 (1985). Colloquially, the balanced comparator is an instrument with a “well-documented Hamiltonian” including its part describing coupling to environment.

⁸⁴ As a reminder, dynamics of this system was discussed in Sec. 2.6 and then again in Sec. 6.1.

where the component states $\rightarrow$ and $\leftarrow$ may be described by wavefunctions localized near the potential well bottoms at $x_s \sim \pm x_0$ – see the blue lines in Fig. 8b. Let us rapidly change the potential profile of the system at $t = 0$, so that at $t > 0$, and near the origin, it may be well approximated by an inverted parabola (see the red line in Fig. 8b):

$$U(x_s) \approx -\frac{m\lambda^2}{2}x_s^2, \quad \text{at } t > 0, \quad |x_s| \ll x_f. \quad (7.219)$$

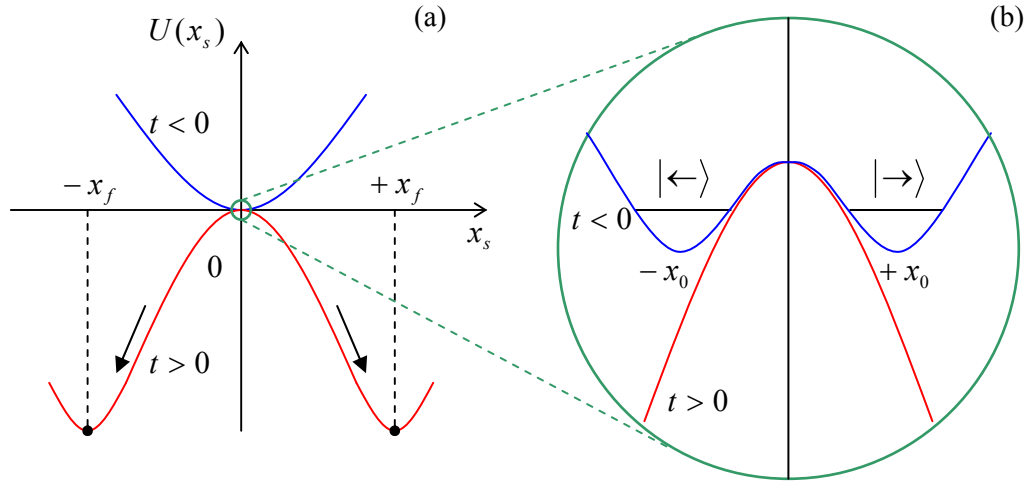


Fig. 7.8. Potential inversion on (a) “macroscopic” and (b) “microscopic” scales of coordinate x .

It is straightforward to verify that the Heisenberg equations of motion in such inverted potential describe an exponential growth of operator $\hat{x}_s$ in time (proportional to $\exp\{\lambda t\}$ and hence a similar growth of the expectation value $\langle x_s \rangle$ and its r.m.s. uncertainty δx_s .⁸⁵ At this “inflation” stage, the coherence between the two component states $\rightarrow$ and $\leftarrow$ is still preserved, i.e. the time evolution is reversible.

Now let the system be weakly coupled to a dissipative (e.g., Ohmic) environment. As we already know, the environment performs two functions. First, it provides motion with viscosity η (141), so that the system would eventually come to rest at one of the relatively distant minima, $\pm x_f$, of the inverted potential (Fig. 8a). Second, the dissipative environment ensures state’s dephasing on some time scale T_2 . If we select the measurement system parameters in such a way that

$$x_0 \ll x_0 \exp\{\lambda T_2\} \ll x_f, \quad (7.220)$$

then the process, after the potential inversion, consists of the following stages, well separated in time:

- the “inflation” stage, preserving the component state coherence but providing an exponential increase of its energy,

⁸⁵ Somewhat counter-intuitively, the latter growth plays a positive role for measurement fidelity. Indeed, it does not affect the intrinsic “signal-to-noise ratio” $\delta x_s / \langle x_s \rangle$, while making the intrinsic (say, quantum-mechanical) uncertainty much larger than possible noise contribution by the latter measurement stage(s).

- the dephasing stage, at which the coherence is suppressed, and the density matrix of the system is reduced to a diagonal form describing the classical mixture of the probability packets propagating to the left and to the right, and

- the stage of settling to a new stationary state – a classical mixture of two states located near points $x_s = \pm x_f$, with probabilities (217) equal to, respectively, $W_{\rightarrow} = |\alpha_{\rightarrow}|^2$ and $W_{\leftarrow} = |\alpha_{\leftarrow}|^2 = 1 - |\alpha_{\rightarrow}|^2$.

If the final states are macroscopically distinguishable (i.e. may play the role of a bistable pointer), as they are in the balanced-comparator implementation, there is absolutely no need, at any of these stages, to involve any mysterious “another mechanism of wavefunction change” (different from the regular, Schrödinger evolution) for the measurement process description.

This may be the only appropriate time to mention, very briefly, the famous - or rather infamous *Schrödinger cat paradox* so much overplayed in popular press. (The only good aspect of this popularity is that the formulation of this paradox is certainly so well known to the reader, that I do not need to repeat it.) In this thought experiment, there is no need to discuss the (rather complex :-)) physics of the cat. As soon as the charged particle, produced at the radioactive decay, reaches the Geiger counter, the process rapidly becomes irreversible, so that the coherent state of the system is reduced to a classical mixture of two possible states: “decay” – “no decay”, leading, correspondingly, to the “cat alive” – “cat dead” states. So, despite attempts by numerous authors, typically without proper physics background, to present this situation as a mystery whose discussion needs the involvement of professional philosophers, hopefully by this point the reader knows enough about dephasing to pay any attention. Let me, however, note the two non-trivial features of this gedanken experiment, that are met in most real experiments as well, including that with the potential inversion (Fig. 8).

First, the role of the measured coordinate of the system under observation (s) may be played not by a coordinate of a single fundamental particle, but a certain combination of coordinates of many microscopic components of a macroscopic body. In particular, in Josephson junction systems such as the balanced comparator we essentially measure the persistent electric current (“supercurrent”) - a certain linear combination of Cartesian components of the momenta of the electrons that constitute the Bose-Einstein condensate of Cooper pairs. At that, the role of the local environment (that contributes significantly to dissipative phenomena) is played by the same electrons, with other linear combinations of electron momenta playing the role of environmental degrees of freedom - which were called $\{\lambda\}$ in the last few sections. This makes the coupling to environment somewhat less apparent (at least for the people who do not know what a linear combination is :-).

Second, one may argue that even after the balanced comparator (in our first example) or the cat (in the second example) has reached its final macroscopic state, human observer’s realization that in this particular experiment the bistable pointer is in a certain state instantly decreases the probability (for the same observer!) of its being in the opposite state to zero. However, as was already discussed in Sec. 2.5, this is a very classical problem of the statistical ensemble redefinition that may be (or may be not) performed at observer’s will. Such redefinition, if performed, is the only possible role of a human (or otherwise intelligent :-)) observer in the measurement process; if we are only interested in an objective recording of results of a pre-fixed series of similar experiments, there is no need to include such observer into any discussion.

The ensemble redefinition at measurement leads to several other paradoxes, of which the so-called *quantum Zeno paradox* is perhaps most spectacular.⁸⁶ Let us return to a two-level system with the unperturbed Hamiltonian given by Eq. (4.166), with $2\pi/\Omega$ much larger than the single-shot measurement time, and the system initially (at $t = 0$) is in a certain quantum well. Then, as we know from Secs. 2.6 and 4.6, before the first measurement, the probability to find state in the initial state at time t is

$$W(t) = \cos^2 \Omega t. \quad (7.221)$$

If the time is small enough ($t = dt \ll 1/\Omega$), we may use the Taylor expansion to write

$$W(dt) \approx 1 - \frac{\Omega^2 dt^2}{4}. \quad (7.222)$$

Now, let us return the two-level system, after its measurement, into the same quantum well, and let it evolve with the same Hamiltonian. Since the occupation of the opposite state is very small, the evolution of W will closely follow the same law as in Eq. (221), but with the initial value given by Eq. (222). Thus, when the system is measured again at time $2dt$,

$$W(2dt) \approx W(dt) \left(1 - \frac{\Omega^2 dt^2}{4} \right) = \left(1 - \frac{\Omega^2 dt^2}{4} \right)^2. \quad (7.223)$$

After repeating this cycle N times (with the total time $t = Ndt$ still much less than $N^{1/2}/\Omega$), the probability that the system is still in the initial state is

$$W(Ndt) \equiv W(t) \approx \left(1 - \frac{\Omega^2 dt^2}{4} \right)^N = \left(1 - \frac{\Omega^2 t^2}{4N^2} \right)^N \approx 1 - \frac{\Omega^2 t^2}{4N}. \quad (7.224)$$

Comparing this result with Eq. (222), we see that the process of system transfer to the opposite quantum well has been slowed down rather dramatically, and in the limit $N \rightarrow \infty$ (at fixed t), its evolution is completely stopped by the measurement process. There is of course nothing mysterious here; the evolution slowdown is due to statistical ensemble's redefinition.

Now let me proceed to question group (ii), in particular to the general issue of the *back action* of the instrument upon the system under measurement (symbolized with the back arrow in Fig. 7). In instruments like the Geiger counter or the balanced comparator, such back action is very large, because the instrument essentially destroys (“demolishes”) the initial state of the system under measurement. However, in the 1970s it was realized that this is not really necessary. In Sec. 3, we have already

⁸⁶ This name, coined by E. Sudarshan and B. Mishra in 1997 (though the paradox had been discussed in detail by A. Turing in 1954); is due to the apparent similarity of this paradox to classical paradoxes by ancient Greek philosopher Zeno of Elea. By the way, just to have a minute of fun, let us have a look what happens when Mother Nature is discussed by people to do not understand math and physics. The most famous of the classical Zeno paradoxes is the *Achilles and Tortoise* case: a fast runner Achilles can apparently never overtake a slower Tortoise, because (in the words by Aristotle) “the pursuer must first reach the point whence the pursued started, so that the slower must always hold a lead”. For a physicist, the paradox has a trivial resolution, but let us listen what a philosopher (D. Burton) writes about it - not in some year BC, but in 2010 AD: “Given the history of ‘final resolutions’, from Aristotle onwards, it’s probably foolhardy to think we’ve reached the end.” For me, this is a sad symbol of modern philosophy.

discussed an example of a two-level system coupled with environment (in our current context, with measurement instrument) and described by Hamiltonian

$$\hat{H} = \hat{H}_s + \hat{H}_{\text{int}} + \hat{H}_e\{\lambda\}, \quad \text{with } \hat{H}_s = a\hat{\sigma}_z, \quad \hat{H}_{\text{int}} = -f\{\lambda\}\hat{\sigma}_z, \quad (7.225)$$

so that

$$[\hat{H}_s, \hat{H}_{\text{int}}] = 0. \quad (7.226)$$

Comparing this equality with Eq. (67) we see that in the Heisenberg picture, the Hamiltonian operator (and hence the energy) of the system of our interest does not change with time. On the other hand, the interaction can change the state of the instrument, so it may be used to measure its energy – or another observable whose operator commutes with the interaction Hamiltonian. Such trick is called either the *quantum non-demolition* (QND) or *back-action-evading* (BAE) measurements.⁸⁷ Let me present a fine example of a real measurement of this kind - see Fig. 9.⁸⁸

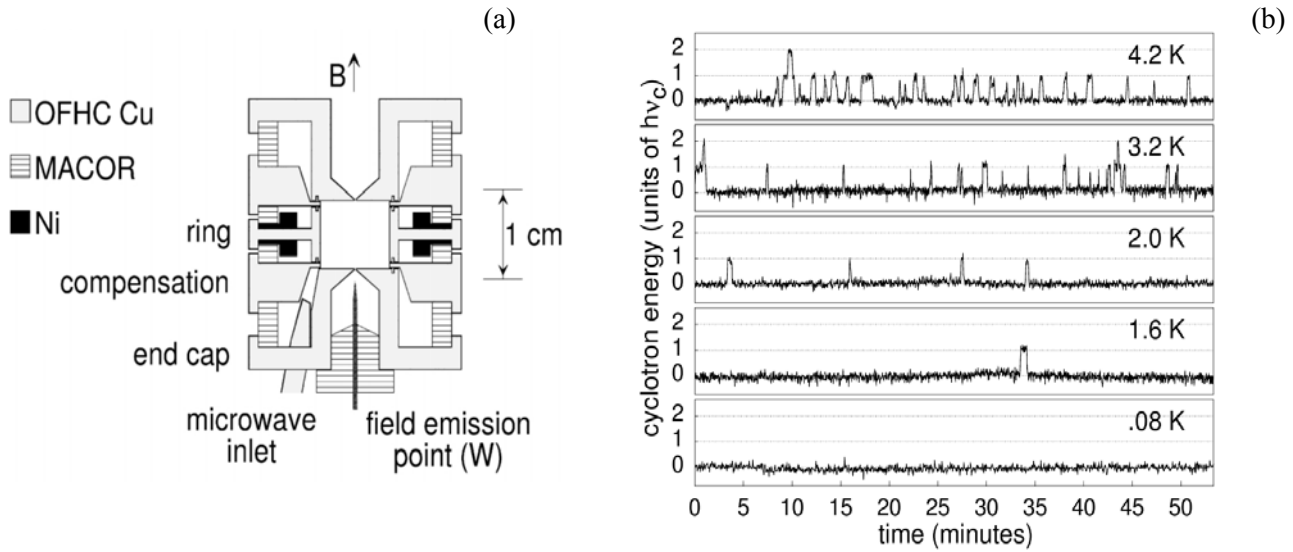


Fig. 7.9. QND measurement of single electron's energy by Peil and Gabrielse: (a) the core of experimental setup, and (b) a record of the thermal excitation and spontaneous relaxation of Fock states. © 1999 APS.

In this experiment, a single electron is captured in a *Penning trap* – a combination of a (virtually) uniform magnetic field $\mathbf{B}$ and a quadrupole electric field.⁸⁹ Such electric field stabilizes cyclotron orbits but does not have any noticeable effect on electron motion in the plane perpendicular to the magnetic field, and hence on its Landau level energies (see Sec. 3.2):

⁸⁷ For a detailed survey of this field see, e.g., either V. Braginsky and F. Khalili, *Quantum Measurements*, Cambridge U. Press, 1992, or H. Wiseman and G. Milburn, *Quantum Measurement and Control*, Cambridge u. Press, 2010.

⁸⁸ S. Peil and G. Gabrielse, *Phys. Rev. Lett.* **83**, 1287 (1999).

⁸⁹ Similar to the one discussed in EM Sec. 2.4 (see in particular Eq. (2.77) and Fig. 2.7), but with additional rotation about one of the axes – either x or y .

$$E_n = \hbar \omega_c \left(n + \frac{1}{2} \right), \quad \text{with } \omega_c = \frac{eB}{m_e}. \quad (7.227)$$

(In the cited work, at $B \approx 5.3$ T, the cyclic frequency $\omega_c/2\pi$ was about 147 GHz, so that the level splitting $\hbar\omega_c$ was close to 10^{-22} J, i.e. corresponded to temperature ~ 10 K, while the physical temperature of the system might be reduced well below that, down to ~ 80 mK). Now note that the analogy between a particle on a Landau levels and a harmonic oscillator goes beyond the energy spectrum. Indeed, since the Hamiltonian of a 2D particle in a perpendicular magnetic field may be reduced to that of a 1D oscillator, we may repeat all procedures of Sec. 5.4 and rewrite it in the terms of creation-annihilation operators:

$$\hat{H}_s = \hbar \omega_c \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right). \quad (7.228)$$

In the Peil and Gabrielse experiment, the electron had one more degree of freedom – along the magnetic field. The electric field of the Penning trap creates a soft confining potential along this direction (vertical in Fig. 9a; let us take it for axis z), so that small electron oscillations along that axis could be well described as a 1D harmonic oscillator of much lower eigenfrequency, in that particular experiment with $\omega_z/2\pi \approx 64$ MHz. This frequency could be measured very accurately (with error ~ 1 Hz) by sensitive electronics whose electric field affects z -motion of the electron, but not its motion in the perpendicular plane. In an exactly uniform magnetic field, the two modes of electron motion would be completely uncoupled. However, the experimental setup included two special superconducting rings made of niobium (Fig. 9a), which slightly distorted the magnetic field and created an interaction between the modes, which might be well approximated by Hamiltonian⁹⁰

$$\hat{H}_{\text{int}} = \text{const} \times \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \hat{z}^2, \quad (7.228)$$

so that the main condition (226) of a QND measurement was well satisfied. At the same time, coupling (228) ensured that a change of the Fock state number n by 1 changed the z -oscillation eigenfrequency by ~ 12.4 Hz. Since this shift was substantially larger than electronics noise, spontaneous changes of n (due to an uncontrolled coupling of the electron to environment) could be readily observed – moreover, continuously monitored – see Fig. 9b. (These data imply that there is virtually no effect of the measuring instrument on the statistics on n – at least on the scale of minutes, i.e. as many as $\sim 10^{13}$ cyclotron orbit periods.) Of course, any measurement – QND or not – cannot avoid the Heisenberg uncertainty relations; in this particular case, a permanent monitoring of the Fock state number n keeps its quantum phase fully uncertain.

It is natural to wonder whether the QND measurement concept may be extended from quadratic forms like the energy to “usual” observables such as coordinates and momenta whose uncertainties are bound by the fundamental Heisenberg’s relation. The answer is yes, but the required methods are a bit more tricky. For example, let us place an electrically charged particle into a uniform electric field $\mathcal{E} = \mathbf{n}_x \mathcal{E}(t)$ of the instrument, so that their interaction Hamiltonian is

⁹⁰ I am simplifying the real situation a bit. Actually, in the experiment there was an electron spin’s contribution to the interaction Hamiltonian as well, but since the large magnetic field polarized the spins quite reliably, their only role was a constant shift of frequency ω_z .

$$\hat{H}_{\text{int}} = -q\hat{\mathcal{E}}(t)\hat{x}. \quad (7.229)$$

Such interaction certainly passes the information on the time evolution of coordinate x to the instrument. However, since Eq. (226) is *not* satisfied - at least for the kinetic-energy part of system's Hamiltonian; as a result the interaction simultaneously distorts the time evolution of particle's momentum. Indeed, writing the Heisenberg equation of motion (4.199) for the x -component of momentum, we get

$$\dot{\hat{p}} - \dot{\hat{p}}|_{\mathcal{E}=0} = q\hat{\mathcal{E}}(t). \quad (7.230)$$

Integrating Eq. (5.169) for the coordinate operator evolution,⁹¹ we get expression,

$$\hat{x}(t) = \hat{x}(0) + \frac{1}{m} \int_0^t \hat{p}(t') dt', \quad (7.231)$$

that shows that the perturbations (230) of the momentum would eventually find their way to the coordinate evolution.

However, for such an important particular system as a harmonic oscillator, the following trick is possible. For this system, Eqs. (5.170) and (230) may be readily combined to give a second-order differential equation for the coordinate operator, that is absolutely similar to the classical equation of motion, and has a similar solution:⁹²

$$\hat{x}(t) = \hat{x}(0) + \frac{q}{m\omega_0} \int_0^t \hat{\mathcal{E}}(t') \sin \omega_0(t - t') dt'. \quad (7.232)$$

This formula confirms that generally the external field $\mathcal{A}(t)$ (in our case, the sensing field of the measurement instrument) affects the time evolution law. Note, however, that if the field is applied only at moments t'_n separated by intervals $T/2$, where $T = 2\pi/\omega_0$ is the oscillation period, its effect on coordinate vanishes at similarly spaced observation instants $t_n = t'_n + (m + 1/2)T$. This is the idea of *stroboscopic* QND measurements. Of course, according to Eq. (230), even such measurement strongly perturbs the oscillator momentum, so that even if values x_n are measured with high accuracy, the Heisenberg's uncertainty relation is not violated.

Experimental implementation of such measurements is not simple (and to the best of my knowledge they have never been successfully demonstrated), but this initial idea has opened a way to more practicable solutions. For example, it is straightforward to use the Heisenberg equations of motion to show that if coupling of two harmonic oscillators, with coordinates x and X , and unperturbed eigenfrequencies ω and Ω , is modulated in time as

$$\hat{H}_{\text{int}} \propto \hat{x}\hat{X} \cos \omega t \cos \Omega t, \quad (7.233)$$

⁹¹ This simple equation is limited to 1D systems with Hamiltonians of the type (2.50), but the reader should agree that this is a pretty general form.

⁹² See, e.g., CM Sec. 4.1. Note in particular that function $\sin \omega_0 \tau$ (with $\tau \equiv t - t'$) under the integral, divided by ω_0 , is nothing more than the temporal Green's function $G(\tau)$, of a loss-free harmonic oscillator.

then the process in one of oscillators (say, that with frequency Ω) does not affect dynamics of one of the *quadrature components* of another oscillator, defined by relations⁹³

$$\hat{x}_1 \equiv \hat{x} \cos \omega t - \frac{\hat{p}}{m\omega} \sin \omega t, \quad \hat{x}_2 \equiv \hat{x} \sin \omega t + \frac{\hat{p}}{m\omega} \cos \omega t, \quad (7.234)$$

while this component's motion does affect the dynamics of one of quadrature components of the counterpart oscillator. (For the counterpart couple of quadrature components, the information transfer goes in the opposite direction.) This scheme has been successfully used for QND measurements in the optical range, with coupling (233) provided by the optical Kerr effect.⁹⁴

Please note that the last two QND measurement examples are based on the idea of *modulation* of a certain parameter in time – either in a short-pulse or sinusoidal form. So, the reader should not be surprised that if the only role of a QND measurement is a sensitive measurement of a weak *classical force* acting on a quantum *probe system*,⁹⁵ i.e. a 1D oscillator of eigenfrequency ω_0 , it may be implemented much simpler – just by modulating the oscillator parameter with frequency $\omega \approx 2\omega_0$. From classical dynamics, we know that if the depth of such modulation exceeds a certain threshold value, it results in excitation of the so-called parametric oscillations with frequency $\omega/2$, and one of two opposite phases.⁹⁶ In the language of Eq. (234), parametric excitation means an exponential growth of one of the quadrature components, with the sign depending on initial conditions, while the counterpart component is suppressed. Close to, but below the excitation threshold, the parameter modulation boosts all perturbations of the almost-excited component (including its quantum-mechanical uncertainty), and suppresses (*squeezes*) those of the counterpart component. The result is a squeezed state, already discussed in Sec. 5.5 above (see in particular Fig. 5.6), that allows one to notice the effect of external force on the oscillator on the backdrop of a quantum uncertainty smaller than the standard quantum limit – see the first of Eqs. (5.174).

In electrical engineering, this fact may be conveniently formulated in terms of *noise parameter* Θ_N of a *linear amplifier* – the instrument for continuous monitoring of an input “signal” – e.g., a microwave or optical waveform.⁹⁷ Namely, Θ_N of “usual” (say, transistor or maser) amplifiers which are equally sensitive to both quadrature components of the signal, Θ_N has a minimum value $\hbar\omega/2$, due to the quantum uncertainty pertinent to the quantum state of the amplifier itself (which therefore plays the role

⁹³ The physical sense of these relations should be clear from Fig. 5.6: they define a system of coordinates rotating clockwise with angular velocity ω , so that the point representing unperturbed classical oscillations with that frequency is at rest in that rotating frame. (The “probability cloud” presenting a Glauber state is also stationary in coordinates $[x_1, x_2]$.) The reader familiar with the classical theory oscillations may notice that x_1 and x_2 are essentially the *RWA variables* u and v , i.e. the *Poincaré plane* coordinates – see, e.g., CM Sec. 4.3-4.6, and especially Fig. 4.9.

⁹⁴ See, e.g., P. Grangier *et al.*, *Nature* **396**, 537 (1998), and references therein. This was, however, not the first QND implementation in optics – for a review see *J. Roch et al.*, *Appl. Phys. B* **55**, 291 (1992).

⁹⁵ As it is, for example, for gravitational wave detectors – see the discussion and references in Sec. 2.10.

⁹⁶ See, e.g., CM Sec. 4.5.

⁹⁷ For the exact definition of the latter parameter, suitable for the quantum sensitivity range ($\Theta_N \sim \hbar\omega$) as well, see, e.g., I. Devyatov *et al.*, *J. Appl. Phys.* **60**, 1808 (1986). In the classical noise limit ($\Theta_N \gg \hbar\omega$), it coincides with $k_B T_N$, where T_N is a more popular measure of electronics noise, called the *noise temperature*.

of its “quantum noise”).⁹⁸ On the other hand, a degenerate parametric amplifier, sensitive to just one quadrature component, may have Θ_N well below $\hbar\omega/2$, due to the squeezing of its ground state.⁹⁹

Finally, let me note that the parameter-modulation schemes of the QND measurements are not limited to harmonic oscillators, and may be applied to other important quantum systems, notably including two-level (i.e. spin- $1/2$ -like) systems.¹⁰⁰

7.8. Exercise problems

7.1. Calculate the density matrix of a two-level system described by Hamiltonian with matrix

$$H = \mathbf{a} \cdot \boldsymbol{\sigma} = a_x \sigma_x + a_y \sigma_y + a_z \sigma_z,$$

where σ_k are the Pauli matrices, and a_k are c -numbers, in thermodynamic equilibrium.

7.2. Find the Wigner function of a harmonic oscillator in:

- (i) at the thermodynamic equilibrium at temperature T ,
- (ii) in the ground state, and
- (ii) in the Glauber state with dimensionless complex amplitude α .

Discuss the relation between the first of the results and the Gibbs distribution.

7.3. Calculate the Wigner function of a harmonic oscillator, with mass m and frequency ω_0 , in its first excited stationary state ($n = 1$).

7.4. Show that the quantum-mechanical Golden Rule (6.111) and the master equation (196) give the same results for the rate of spontaneous quantum transitions $n' \rightarrow n$ in a system with discrete energy spectrum, weakly coupled to a low-temperature the heat bath ($k_B T \ll \hbar\omega_{nn'}$).

Hint: Try to establish a relation between function $\text{Im}\chi(\omega_{nn'})$ that participates in Eq. (196), and the density of states ρ_n that participates in the Golden Rule formulas, by considering a particular case of sinusoidal oscillations in the system of interest.

7.5.* A harmonic oscillator is weakly coupled to an Ohmic environment.

(i) Use the rotating-wave approximation to write equations of motion for the Heisenberg operators of the complex amplitude of oscillations.

(ii) Calculate the expectation values of the correlators of the fluctuation force operators, participating in these equations, and express them via the average number $\langle n \rangle$ of thermally-induced excitations in equilibrium, given by the second of Eqs. (26b).

7.6. For a harmonic oscillator with weak Ohmic dissipation:

- (i) Spell out the system of differential equations for the energy level occupancies W_n .

⁹⁸ This fact was recognized very early – see, e.g., H. Haus and J. Mullen, *Phys. Rev.* **128**, 2407 (1962).

⁹⁹ See, e.g., the spectacular experiments by B. Yurke *et al.*, *Phys. Rev. Lett.* **60**, 764 (1988).

¹⁰⁰ See, e.g., D. Averin, *Phys. Rev. Lett.* **88**, 207901 (2002).

- (ii) Use this system to find the time evolution of the expectation value $\langle E \rangle$ of oscillator's energy.
- (iii) Compare the last result with that following from the Heisenberg-Langevin approach.

7.7. Derive Eq. (209) in an alternative way, using an expression dual to Eq. (5.28b).

7.8. * A particle in a system of two coupled quantum wells (see, e.g., Fig. 4) is weakly coupled to an Ohmic environment.

- (i) Derive the equations of time evolution of the density matrix elements.
- (ii) Solve these equations in the low-temperature limit, when the energy level splitting is much larger than $k_B T$, to calculate the time evolution of the probability $W_L(t)$ of finding the particle one of the wells, after it had been placed there at $t = 0$.

7.9. * A spin- $1/2$ particle is placed into magnetic field $\mathcal{B}(t) = \mathcal{B}_0 + \tilde{\mathcal{B}}(t)$ with an arbitrary but small time-dependent component ($|\tilde{\mathcal{B}}| \ll |\mathcal{B}_0|$), and is also weakly coupled to dissipative environment. Derive the differential equations describing the time evolution of the expectation values ($\langle S_x \rangle$, etc.) of spin's Cartesian components.

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Chapter 8. Multiparticle Systems

This chapter is a brief introduction to quantum mechanics of systems of similar particles, with a special attention to the case when they are indistinguishable. For such systems, the theory predicts (and experiment confirms) very specific effects even in the case of negligible explicit (“direct”) interaction between the particles. The effects notably include the Bose-Einstein condensation of bosons, and the Pauli exclusion principle and exchange interaction for fermions.

8.1. Distinguishable and indistinguishable particles

The importance of quantum systems of many similar particles is probably self-evident; just the very fact of that most atoms include several/many electrons is sufficient to attract our attention. There are also important systems where the number of electrons is much higher than in one atom; for example, a cubic centimeter of a typical metal features $\sim 10^{23}$ conduction electrons that cannot be attributed to particular atoms, and have to be considered as common (and interacting!) parts of the system as the whole. Though quantum mechanics offers virtually no exact analytical solutions for systems of strongly interacting particles,¹ it reveals very important new effects even in the simplest case when particles do not interact, and least explicitly (*directly*).

If non-interacting particles are either different from each other by their nature (say, an electron and a proton), or physically similar but still *distinguishable* because of other reasons (say, because of their reliable spatial separation) everything is simple – at least, conceptually. Then, as was already discussed in Sec. 6.7, a system of two particles, 1 and 2, each in a pure quantum state, may be described by a ket vector

$$|\alpha\rangle = |\beta\rangle_1 \otimes |\beta'\rangle_2, \quad (8.1a)$$

Pure state
of 2
distinguish-
able
particles

where the single-particle states β and β' are defined in different Hilbert spaces. (Below, I will frequently use the following convenient shorthand,

$$|\alpha\rangle = |\beta\beta'\rangle, \quad (8.1b)$$

in which the state position within a vector codes the particle number.) Hence the *permuted state*

$$\hat{\mathcal{P}} |\beta\beta'\rangle \equiv |\beta'\beta\rangle = |\beta'\rangle_1 \otimes |\beta\rangle_2, \quad (8.2)$$

where $\hat{\mathcal{P}}$ is the *permutation operator*, is clearly different from the initial one.

¹ An important conceptual question is why not treat one particle of such a collection as an open quantum system, and apply to it the powerful methods discussed in the last chapter, based on the separation of the whole Nature into the “system of our interest” and the “environment” – see Fig. 7.1. Such separation is very natural and works very well in cases when one, relative “massive” (inertial) particle, or a specific collective degree of freedom (also relatively inertial), is surrounded by a sea of “lighter particles”, which serve the role of an environment – frequently in or close to thermal equilibrium. On the other hand, in most systems of identical particles, such separation is more artificial and may lead to errors, because the quantum state of the “particle of interest” may be substantially correlated (in particular, entangled) with that of similar particles of its “environment” – see the discussion later in this section.

Again, such description is valid even for *identical* particles if they are still *distinguishable* by their spatial separation. (The separation does not preclude particles from interacting with each other, e.g., electrostatically.) Such systems of similar but clearly distinguishable particles (or subsystems) are broadly discussed nowadays, for example in the context of quantum computing and encryption – see Sec. 8.5 below. This is why it is unfortunate that term “identical particles” is frequently used in the sense of *indistinguishable* particles. I will try to avoid this confusion by using the latter term, despite it being rather unpleasant grammatically.

Now comes the most important *experimental fact*: identical elementary particles,² if they are not reliably separated, are genuinely *indistinguishable*, i.e. their Hilbert spaces are not separable. Hence, instead of Eq. (1), for a set of two particles, we need to use a linear combination of products like $|\beta\beta'\rangle$ and $|\beta'\beta\rangle$ for the construction of genuine quantum states.³ In order to comprehend what exactly linear combinations should be used, it is convenient to discuss properties of the permutation operator defined by the first of Eqs. (2).

Let us consider an observable A , and a system of eigenstates of its operator:

$$\hat{A}|a_j\rangle = A_j|a_j\rangle. \quad (8.3)$$

If the particles are indistinguishable indeed, the observable expectation value should not be affected by their permutation. Hence operators $\hat{A}$ and $\hat{\mathcal{P}}$ have to commute, and share their eigenstates. This is why eigenstates of operator $\hat{\mathcal{P}}$ are so important: in particular, they are also eigenstates of the Hamiltonian, i.e. the stationary states of the system of particles.

Now let us have a look at the operation described by the square of the permutation operator, on an elementary ket-vector product:

$$\hat{\mathcal{P}}^2|\beta\beta'\rangle = \hat{\mathcal{P}}(\hat{\mathcal{P}}|\beta\beta'\rangle) = \hat{\mathcal{P}}|\beta'\beta\rangle = |\beta\beta'\rangle, \quad (8.4)$$

² Here by “elementary particles” I mean any of the following two options:

(i) particles like electrons, which (at least at this stage of development of physics) are considered as structure-less entities;

(ii) any object (e.g., a hadron or meson) which may be considered as a system of “more elementary” particles (e.g., quarks), but still may be reliably placed in a definite (say, ground) quantum state.

From that point of view, even complex atoms or molecules of a certain chemical element, each in its ground state, may be considered on the same footing as elementary particles.

³ A very legitimate question is why, in this situation, we need to introduce particle’s number to start with. A partial answer is that in this approach it is much simpler to derive (or guess) problem Hamiltonians from the correspondence principle. For example for a system of two spinless particles, each in an external potential $U(\mathbf{r})$, and with the interaction energy $U_{\text{int}}(|\mathbf{r}_1 - \mathbf{r}_2|)$, the correct Hamiltonian is

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + U(\hat{\mathbf{r}}_1) + U(\hat{\mathbf{r}}_2) + U_{\text{int}}(|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|).$$

Later in this chapter, we will discuss an alternative approach (the so-called “second quantization”) in which tracing a certain particle is avoided. While for indistinguishable particles this is more logical, in that approach writing adequate Hamiltonians (which, in particular, would avoid spurious self-interaction of the particles) is much more challenging – see Sec. 3 below.

i.e. $\hat{\mathcal{P}}^2$ brings the state back to its original form. Since any pure state of a two-particle system may be represented as a linear combination of such products, this result does not depend on the state, and may be represented as an operator relation:

$$\hat{\mathcal{P}}^2 = \hat{I}. \quad (8.5)$$

Now let us find the possible eigenvalues $\mathcal{P}_j$ of the permutation operator. Acting by both sides of Eq. (5) on any of eigenstates $|\alpha_j\rangle$ of the permutation operator, we get a very simple equation for its eigenvalues:

$$\mathcal{P}_j^2 = 1, \quad (8.6)$$

with two possible solutions:

$$\mathcal{P}_j = \pm 1. \quad (8.7)$$

Let us find the eigenstates of the permutation operator in the simplest case when each of the component particles can be only in two single-particle states - say, β and β' . Evidently, none of the simple products $|\beta\beta'\rangle$ and $|\beta'\beta\rangle$, taken alone, does qualify for the eigenstate - unless states β and β' are identical. Let us try their linear combination

$$|\alpha_j\rangle = a|\beta\beta'\rangle + b|\beta'\beta\rangle, \quad (8.8)$$

so that

$$\hat{\mathcal{P}}|\alpha_j\rangle = \mathcal{P}_j|\alpha_j\rangle = a|\beta'\beta\rangle + b|\beta\beta'\rangle. \quad (8.9)$$

For the case $\mathcal{P}_j = +1$ we have to require states (8) and (9) to be the same, so that $a = b$. Assuming also that the single-particle states β and β' are normalized, and requiring the same for the composite state α , we get the so-called *symmetric eigenstate*⁴

$$|\alpha_+\rangle = \frac{1}{\sqrt{2}}(|\beta\beta'\rangle + |\beta'\beta\rangle). \quad (8.10)$$

Similarly, for $\mathcal{P}_j = -1$ we get $a = -b$, and the *antisymmetric eigenstate*

$$|\alpha_-\rangle = \frac{1}{\sqrt{2}}(|\beta\beta'\rangle - |\beta'\beta\rangle). \quad (8.11)$$

where the front coefficients guarantee the orthonormality of the two-particle states, provided that the single-particle states are orthonormal. These are typical examples of *entangled states*, defined as multi-particle states whose state vectors cannot be factored into a product of single-particle vectors.

So far, our math does not preclude either sign of $\mathcal{P}_j$, in particular the possibility that the sign depends on the state (i.e. index j). Here, however, comes in another crucial experimental fact: all elementary particles fall into two groups:⁵

⁴ As in many situations we met before, kets (10) and (11) may be multiplied by $\exp\{i\varphi\}$ with an arbitrary real phase φ . However, until we discuss coherent superpositions of various states α , there is no good motivation for taking the phase different from 0; that would only clutter the notation.

- (i) *bosons*, particles with integer spin s , for which $\mathcal{P}_j = +1$ for any j , and
- (ii) *fermions*, particles with half-integer spin, with $\mathcal{P}_j = -1$, also for any j .

In the nonrelativistic theory we are discussing now, this key fact should be considered as experimental one. (The relativistic quantum theory, to be discussed in Chapter 9, offers a proof that half-integer-spin particles cannot be bosons and integer-spin ones cannot be fermions, but not more than that.) However, our discussion of spin in Sec. 5.7 allows the following *interpretation* of the fermion-boson difference. In free space, the permutation of particles 1 and 2 may be viewed as a result of rotation of this pair by angle $\pm\pi$ about a certain axis. As we have seen in Sec. 5.7, at a rotation by such an angle, the state vector $|\beta\rangle$ of a particle with quantum number m_s (that ranges from $-s$ to $+s$, and hence may take only integer values for integer s , and only half-integer values for half-integer s) changes by factor $\exp\{\pm i\pi m_s\}$, so that the state product $|\beta\beta\rangle$ changes by $\exp\{\pm i2\pi m_s\}$, i.e. by factor $+1$ for integer s , and by factor (-1) for half-integer s .

Since eigenvalues P_j do not depend on the particular state of the system, we can write explicit expressions for the permutation operator:

$$\hat{\mathcal{P}} = \hat{I} \times \begin{cases} +1, & \text{for bosons,} \\ -1, & \text{for fermions.} \end{cases} \quad (8.12)$$

The most impressive corollaries of Eqs. (10) and (11) are for the case when the partial states of the two particles are the same: $\beta = \beta'$. The corresponding Bose state α_+ is possible; in particular, at sufficiently low temperatures, a set of non-interacting Bose particles condenses on the ground state of each of them – the so-called *Bose-Einstein condensate* (“BEC”).⁶ Its examples include superfluid fluids like helium, the Cooper-pair condensate in superconductors, and the BEC of weakly interacting atoms. Perhaps the most fascinating feature of a multiparticle Bose-Einstein condensate is that dynamics of its observables is governed by laws of quantum mechanics, while (for nearly all purposes) may be treated as *c*-numbers – see, e.g., Eqs. (2.54)-(2.55).⁷

On the other hand, if we take $\beta = \beta'$ in Eq. (11), we see that state α_- vanishes, i.e. *cannot exist* at all. This is the mathematical expression of the *Pauli exclusion principle*: two indistinguishable fermions cannot be in the same quantum state.⁸ (As will be discussed below, this is true for systems with more than two fermions as well.) Probably, the key importance of this principle is self-evident: if it was not valid for electrons (that are fermions), all electrons of each atom would condense on its ground ($1s$) level, and all the usual chemistry (and biochemistry, and biology, including dear us!) would not exist. The Pauli principle effectively makes fermions interacting even if they do not interact directly, in the usual sense of this word.

⁵ Traditionally, people speak about two different “statistics”: the *Bose-Einstein statistics* of bosons, and *Fermi-Dirac statistics* of fermions, because their statistical distributions in thermal equilibrium are indeed different – see, e.g., SM Sec. 2.8. However, as evident from the above discussion, their difference is deeper, and actually we are dealing with *two different quantum mechanics*.

⁶ For a quantitative discussion of the Bose-Einstein condensation see, e.g., SM Sec. 3.4.

⁷ Such possibility follows from the fact that for the Bose-Einstein condensate of $N \gg 1$ particles, the Heisenberg uncertainty relation may be reduced to $\delta N \delta \varphi > 1$, where φ is the condensate wavefunction’s phase, so that it may have $\delta N / \langle N \rangle \ll 1$ and $\delta \varphi \ll 1$ simultaneously.

⁸ It was formulated by W. Pauli in 1925, on the basis of less general rules suggested by G. Lewis (1916), I. Langmuir (1919), N. Bohr (1922), and E. Stoner (1924) for the explanation of experimental spectroscopic data.

8.2. Singlets, triplets, and the exchange interaction

Now let us discuss possible approaches to analysis of identical particles on a simple but very important example of a pair of spin- $\frac{1}{2}$ particles (say, electrons) whose interaction with either each other or the external world does not involve spin. Then the ket-vector of a total state is factorable as

$$|\alpha_-\rangle = |o_{12}\rangle \otimes |s_{12}\rangle, \quad (8.13)$$

with the orbital function $|o_{12}\rangle$ and the spin function $|s_{12}\rangle$ (that depends on the state of both spins of the pair) belonging to different Hilbert spaces. It is frequently convenient to use the coordinate representation of such state, sometimes called the *spinor*:

2-particle
spinor

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \alpha_- \rangle = \langle \mathbf{r}_1, \mathbf{r}_2 | o_{12} \rangle \otimes |s_{12}\rangle \equiv \psi(\mathbf{r}_1, \mathbf{r}_2) |s_{12}\rangle. \quad (8.14)$$

Since spin- $\frac{1}{2}$ particles are fermions, the particle permutation,

$$\hat{P}\psi(\mathbf{r}_1, \mathbf{r}_2) |s_{12}\rangle = \psi(\mathbf{r}_2, \mathbf{r}_1) |s_{21}\rangle = -\psi(\mathbf{r}_1, \mathbf{r}_2) |s_{12}\rangle, \quad (8.15)$$

has to change the sign of either the spin part or the orbital factor of the spinor. In the case of a symmetric orbital factor,

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2), \quad (8.16)$$

the spin factor has to obey relation

$$|s_{21}\rangle = -|s_{12}\rangle. \quad (8.17)$$

Let us use the ordinary z -basis (where z , in the absence of external magnetic field, is an arbitrary spatial axis) for each of the spins. In this basis, any ket-vector $|m_s\rangle$ of spin orientation of two particles may be represented as a linear combination of four single-spin basis vectors:

$$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, \text{ and } |\downarrow\uparrow\rangle. \quad (8.18)$$

The first two kets evidently do not satisfy Eq. (17), and cannot participate in the state. Applying to the remaining kets the same argumentation as has resulted in Eq. (11), we get

Singlet
state

$$|s_{12}\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (8.19)$$

Such orbital-symmetric and spin-asymmetric state is called the *singlet*. The origin of this name becomes clear from the analysis of the opposite (orbital-asymmetric and spin-symmetric) case:

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = -\psi(\mathbf{r}_1, \mathbf{r}_2), \quad |s_{12}\rangle = |s_{21}\rangle. \quad (8.20)$$

For the composition of such symmetric spin state, the first two kets of Eq. (18) are completely acceptable (with arbitrary weights), and so is a specific symmetric combination of two last kets, similar to Eq. (10):

Triplet
states

$$|s_{12}\rangle = c_+ |\uparrow\uparrow\rangle + c_- |\downarrow\downarrow\rangle + c_0 \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle). \quad (8.21)$$

We may use this composite state with any values of coefficients c (satisfying the normalization condition), because they correspond to the same orbital wavefunction and hence the same energy. However, each of these three states has a specific value of the z -component of the net spin (respectively, $+\hbar$, $-\hbar$, and 0).⁹ Because of this, an even small external magnetic field lifts their degeneracy, splitting the energy level in three, and giving it the natural name of *triplet*.

In the particular case when the particles do not interact at all, for example¹⁰

$$\hat{H} = \hat{h}_1 + \hat{h}_2, \quad \hat{h}_k = \frac{\hat{p}_k^2}{2m} + \hat{U}(\mathbf{r}_k), \quad k = 1, 2, \quad (8.22)$$

the 2-particle Schrödinger equation for the symmetrical orbital wavefunction (16) is obviously satisfied by the simple product,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_n(\mathbf{r}_1)\psi_{n'}(\mathbf{r}_2), \quad (8.23)$$

of single-particle eigenfunctions, with arbitrary sets n, n' of quantum numbers. For the particular (but very important!) case $n = n'$, this means that the eigenenergy of the singlet state,

$$\frac{1}{\sqrt{2}}\psi_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right), \quad (8.24)$$

is just $2\varepsilon_n$, where ε_n is the single-particle energy level. It may be proved that the lowest energy of the triplet state is always higher than that. Hence, for the limited (but extremely important!) goal of finding ground-state energies of multi-electron systems, we may ignore the actual singlet structure of spinor (24), and reduce the Pauli exclusion principle to the semi-qualitative picture of single-particle levels, each “occupied” with 2 independent particles.

As a very simple example, let us find the ground energy of a deep, cubic-shaped, 3D quantum well with side a , filled with 5 fermions, ignoring their direct interaction. From the solution of the single-particle Schrödinger equation in Sec. 1.5, we know the single-particle energy spectrum of the system:

$$\varepsilon_{n_x, n_y, n_z} = \varepsilon_0(n_x^2 + n_y^2 + n_z^2), \quad \text{with } \varepsilon_0 \equiv \frac{\pi^2 \hbar^2}{2ma^2}, \quad \text{and } n_x, n_y, n_z = 1, 2, \dots \quad (8.25)$$

so that the lowest-energy orbital states are:

- one ground state with $\{n_x, n_y, n_z\} = \{1, 1, 1\}$, and energy $\varepsilon_{111} = (1^2 + 1^2 + 1^2)\varepsilon_0 = 3\varepsilon_0$, and
- three excited states, with $\{n_x, n_y, n_z\}$ equal to $\{2, 1, 1\}$, $\{1, 2, 1\}$, and $\{1, 1, 2\}$, with equal energies $\varepsilon_{211} = \varepsilon_{121} = \varepsilon_{112} = (2^2 + 1^2 + 1^2)\varepsilon_0 = 6\varepsilon_0$.

According to the Pauli principle, each of these energy levels states can accommodate up to 2 electrons. Hence the lowest-energy (ground) state of the 5-electron system is achieved by placing 2 of

⁹ Note that in the sense of Eq. (5.197), all three triplet states of a two-electron system behave as a single integer spin with $s = 1$; for example, S^2 equals $2\hbar^2$, rather than 0 as one could expect for the last component of Eq. (21) – see Problem 1.

¹⁰ In this chapter, I try to use lower-case letters for observables of single particles (in particular, ε for their energies), in order to distinguish them as clearly as possible from system’s variables, including the total energy E of the system, typeset in capital letters.

them on the ground level $\varepsilon_{111} = 3\varepsilon_0$, and the remaining 3 particles, in any of the degenerate “excited” states of energy $6\varepsilon_0$. Hence the ground energy of the system is

$$E_g = 2 \times 3\varepsilon_0 + 3 \times 6\varepsilon_0 = 24\varepsilon_0 = \frac{12\pi^2 \hbar^2}{ma^2}. \quad (8.26)$$

In many cases of relatively weak interaction between particles, it does not blow up such a simple quantum state classification scheme, and the Pauli principle allows tracing the order of single-particle state filling with Fermi particles. This is exactly the approach that has been used at our discussion of atoms in Sec. 3.7.

Now let us describe the results of particle interaction more quantitatively, on the simplest example¹¹ of the lowest energy states of a neutral atom¹² of helium - more exactly, helium-4, usually denoted ${}^4\text{He}$, consisting of a nucleus with two protons and two neutrons, of the total electric charge $q = +2e$, and two electrons “rotating” about it. Neglecting the small relativistic effects that was discussed in Sec. 6.3, the Hamiltonian describing the electron motion may be represented as

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{u}_{\text{int}}, \quad \hat{h}_k = \frac{\hat{p}_k^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_k}, \quad \hat{u}_{\text{int}} = \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}. \quad (8.27)$$

As most problems of multiparticle quantum mechanics, the eigenvalue/eigenstate problem for this Hamiltonian does not have an exact analytical solution, so let us start an approximate analysis considering the electron-electron interaction as a perturbation. As was discussed in Chapter 6, we have to start with the “0th-order” approximation in which the perturbation is ignored, so that the Hamiltonian is reduced to sum (22). In this approximation, the ground state g of the atom is the singlet (24), with the orbital factor

$$\psi_g(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \quad (8.28)$$

and energy $2\varepsilon_g$. Here each operand $\psi_{100}(\mathbf{r})$ is the single-particle wavefunction of the ground ($1s$) state of the hydrogen-like atom with $Z = 2$, with quantum numbers $n = 1, l = 0, m = 0$. According to Eqs. (3.174) and (3.198),

$$\psi_{100}(\mathbf{r}) = Y_0^0(\theta, \varphi) \mathcal{R}_{1,0}(r) = \frac{1}{\sqrt{4\pi}} \frac{2}{r_0^{3/2}} e^{-r/r_0}, \quad \text{with } r_0 = \frac{r_B}{Z} = \frac{r_B}{2}, \quad (8.29)$$

so that according to Eq. (3.191), in this approximation the total ground state energy is

$$E_g^{(0)} = 2\varepsilon_g^{(0)} = 2 \left(-\frac{\varepsilon_0}{2n^2} \right)_{n=1, Z=2} = 2 \left(-\frac{Z^2 E_H}{2} \right)_{Z=2} = -4E_H \approx -109 \text{ eV}. \quad (8.30)$$

This is still somewhat far (though not terribly far!) from the experimental value $E_g \approx -78.8 \text{ eV}$ – see the bottom level in Fig. 1a.

¹¹ It is also very important, since helium makes up more than 20% of all “ordinary” matter of our Universe.

¹² Evidently, the positive ion He^{+1} of such atom, with just one electron, is very well described by the hydrogen-like atom theory with $Z = 2$, whose ground-state energy, according to Eq. (3.191), is $-Z^2 E_H/2 = -2E_H \approx -55.4 \text{ eV}$.

Making a small detour from our main topic, electron indistinguishability effects, let us note that we can get a much better agreement with experiment by calculating the electron interaction energy in the 1st order of the perturbation theory. Indeed, in application to our system, Eq. (6.13) reads

$$E_g^{(1)} = \langle g | \hat{u}_{\text{int}} | g \rangle = \int d^3 r_1 \int d^3 r_2 \psi_g^*(\mathbf{r}_1, \mathbf{r}_2) u_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) \psi_g(\mathbf{r}_1, \mathbf{r}_2). \quad (8.31)$$

Plugging in Eqs. (27)-(29), we get

$$E_g^{(1)} = \left(\frac{1}{4\pi} \frac{4}{r_0^3} \right)^2 \int d^3 r_1 \int d^3 r_2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \exp\left\{ -\frac{2(r_1 + r_2)}{r_0} \right\}. \quad (8.32)$$

As may be readily evaluated analytically (this exercise is left for the reader), this expression equals $(5/4)E_H$, so that the corrected ground state energy,

$$E_g \approx E_g^{(0)} + E_g^{(1)} = \left(-4 + \frac{5}{4} \right) E_H = -74.8 \text{ eV}, \quad (8.33)$$

is much closer to experiment.

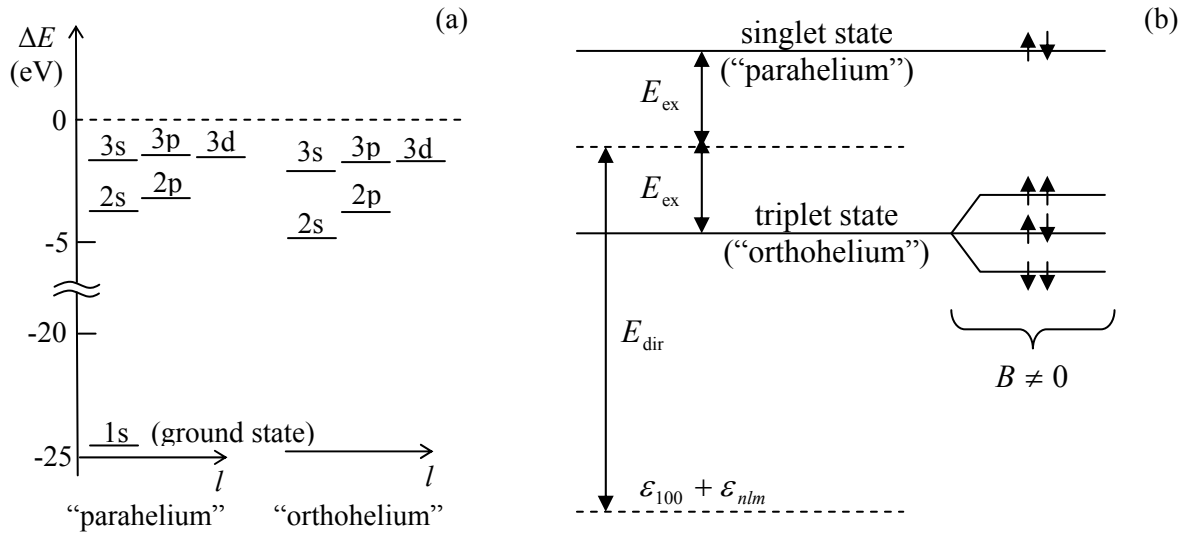


Fig. 8.1. The lowest energy levels of a helium atom: (a) experimental data and (b) a schematic structure of an excited state with fixed n and l in the first order of the perturbation theory. On panel (a), all energies are referred to that $(-2E_H \approx -55.4 \text{ eV})$ of the ground state of ion He^{+1} , so that their magnitudes are the (readily measurable) energies of atom's ionization starting from the corresponding bound state.

There is still a room for improvement - that may be made, for example, using the *variational method*,¹³ based on the following, very general observation. Let n be the exact, full and orthonormal set of stationary states of a quantum system, and use it as the basis for expansion of a normalized but otherwise arbitrary *trial state* α (defined in the same Hilbert space):

$$|\alpha\rangle = \sum_n \alpha_n |n\rangle, \quad (8.34)$$

¹³ See also Problems 2.6-2.8, 2.34, and 3.3.

with the energy that may be calculated using the general (4.125):

$$E_\alpha = \langle \alpha | \hat{H} | \alpha \rangle = \sum_n W_n E_n, \quad \text{where } W_n = |\alpha_n|^2 \geq 0. \quad (8.35)$$

Since, by definition, the exact ground state energy E_g is the lowest one of the set E_n , we can use Eq. (35) to compose the following inequality:

Variational
method's
justification

$$E_\alpha \geq \sum_n W_n E_g = E_g \sum_n W_n = E_g. \quad (8.36)$$

Thus, the ground state energy is always lower then (or equal to) the energy of any trial state α . Hence, if we make several attempts with reasonably selected trial states, we may expect the lowest of the results to approximate the genuine ground state energy reasonably well.

For our particular case of a ^4He atom, we may try to use, as the trial state, the wavefunction given by Eqs. (28)-(29), but with the atomic number Z considered as an adjustable parameter $Z_{\text{ef}} < Z = 2$ rather than a fixed number. The physics behind this idea is that each the electric charge density $\rho(\mathbf{r}) = -e|\psi(\mathbf{r})|^2$ of each electron forms a negatively charged “cloud” that reduces the effective charge of the nuclei, as seen by another electron, to $Z_{\text{ef}}e^2$, with some $Z_{\text{ef}} < 2$. As a result, the single-particle wavefunction spreads further in space ($r_0 = r_B/Z_{\text{ef}} > r_B/Z$), while keeping its functional form (29) nearly intact. Since the kinetic energies T in system's Hamiltonian are proportional to r_0^{-2} , while the potential energies scale as r_0^{-1} , we can write

$$E_g(Z_{\text{ef}}) = \left(\frac{Z_{\text{ef}}}{2} \right)^2 \langle T_g \rangle_{Z=2} + \frac{Z_{\text{ef}}}{2} \langle U_g \rangle_{Z=2}. \quad (8.37)$$

Now we can use the fact that according to Eq. (3.202), for any stationary state of a hydrogen-like atom (just as for the classical circular motion in the Coulomb potential), $\langle U \rangle = 2E$, and hence $\langle T \rangle = E - \langle U \rangle = -E$. Using Eq. (8.30), and adding the correction $U_g^{(1)} = -(5/4)E_H$ calculated above, to the potential energy, we get

$$E_g(Z_{\text{ef}}) = \left[4 \left(\frac{Z_{\text{ef}}}{2} \right)^2 + \left(-8 + \frac{5}{4} \right) \frac{Z_{\text{ef}}}{2} \right] E_H. \quad (8.38)$$

The minimum of function $E_g(Z_{\text{ef}})$ and the corresponding “optimal” value of Z_{ef} are as follows:

$$(Z_{\text{ef}})_{\text{opt}} = 2 \left(1 - \frac{5}{32} \right) = 1.6875, \quad (E_g)_{\text{min}} \approx -2.85 E_H \approx -77.5 \text{ eV}. \quad (8.39)$$

Given the trial function crudeness, this number is in a surprisingly good agreement with experimental value cited above, with a difference of the order of 1%.¹⁴

Now let us return of our basic topic – the effects of electron indistinguishability. As we have just seen, the ground level energy of the helium atom is not affected directly by this fact, but the situation is

¹⁴ This example explains why the variational method is broadly used for approximate treatment of complex quantum systems, although it is based more or less intuitive guesses of trial functions, i.e. in contrast with the perturbation theories discussed in Chapters 6 and 7, does *not* guarantee asymptotically correct results in any particular limit, unless such correctness is manually incorporated into the trial state choice.

different for its excited states – even the lowest ones. The reasonably good convergence of the perturbation theory, that we have seen for the ground state, tells us that we can base our analysis of wavefunctions (ψ_e) of the lowest excited state orbitals, on products like $\psi_{100}(\mathbf{r}_k)\psi_{nlm}(\mathbf{r}_k)$, with $n > 1$. However, in order to satisfy the fermion permutation rule, $\mathcal{P}_j = -1$, we have to take the orbital part of the state in an either symmetric or asymmetric form:

$$\psi_e(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)] \quad (8.40)$$

Orbital
functions of
orthohelium
and
parahelium

with the proper total permutation asymmetry provided by the corresponding spin part given by, respectively, Eq. (19) or Eq. (21), so that the upper/lower signs in Eq. (40) correspond to the singlet/triplet spin state. Let us calculate the expectation values of the total energy of the system in the first order of the perturbation theory. Plugging Eq. (40) into the 0th order expression

$$\langle E_e \rangle^{(0)} = \int d^3r_1 \int d^3r_2 \psi_e^*(\mathbf{r}_1, \mathbf{r}_2) (\hat{H}_1 + \hat{H}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2), \quad (8.41)$$

we get two groups of similar terms that differ only by the particle index. We can merge the terms of each pair by changing the notation as ($\mathbf{r}_1 \rightarrow \mathbf{r}$, $\mathbf{r}_2 \rightarrow \mathbf{r}'$) in one of them, and ($\mathbf{r}_1 \rightarrow \mathbf{r}'$, $\mathbf{r}_2 \rightarrow \mathbf{r}$) in the other term. Using Eq. (27), and the mutual orthogonality of wavefunctions $\psi_{100}(\mathbf{r})$ and $\psi_{nlm}(\mathbf{r})$, we get the following result,

$$\begin{aligned} \langle E_e \rangle^{(0)} &= \int \psi_{100}^*(\mathbf{r}) \left(-\frac{\hbar^2 \hat{\nabla}_{\mathbf{r}}^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r} \right) \psi_{100}(\mathbf{r}) d^3r + \int \psi_{nlm}^*(\mathbf{r}') \left(-\frac{\hbar^2 \hat{\nabla}_{\mathbf{r}'}^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r'} \right) \psi_{nlm}(\mathbf{r}') d^3r' \\ &= \varepsilon_{100} + \varepsilon_{nlm}, \end{aligned} \quad (8.42)$$

which may be interpreted as the sum of eigenenergies of two separate single particles, one in the ground state 100, and another in the excited state nlm - despite that actually the electron states are entangled. Thus, in the 0th order of the perturbation theory, the electron entanglement does not affect their energy.

However, the potential energy of the system also includes the interaction term U_{int} (27) that does not allow such separation. As a result, in the first approximation of the perturbation theory, the total energy of the system may be represented as

$$E_e = \varepsilon_{100} + \varepsilon_{nlm} + E_{\text{int}}^{(1)}, \quad (8.43a)$$

$$E_{\text{int}}^{(1)} = \langle U_{\text{int}} \rangle = \int d^3r_1 \int d^3r_2 \psi_e^*(\mathbf{r}_1, \mathbf{r}_2) U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2) \quad (8.43b)$$

Plugging Eq. (40) into this result, using the symmetry of u_{int} with respect to the particle number permutation, and the same particle coordinate re-numbering as above, we get

$$E_{\text{int}}^{(1)} = E_{\text{dir}} \pm E_{\text{ex}}, \quad (8.44)$$

with deceptively similar expressions for the operands:

$$E_{\text{dir}} \equiv \int d^3r \int d^3r' \psi_{100}^*(\mathbf{r}) \psi_{nlm}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_{100}(\mathbf{r}) \psi_{nlm}(\mathbf{r}'), \quad (8.45a)$$

$$E_{\text{ex}} \equiv \int d^3r \int d^3r' \psi_{100}^*(\mathbf{r}) \psi_{nlm}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_{nlm}(\mathbf{r}) \psi_{100}(\mathbf{r}'). \quad (8.45b)$$

Exchange
interaction
energy

Since the single-particle orbitals can be always made real, both components are positive (or at least non-negative). However, their physics is completely different. Integral (45a), called the *direct* electron-electron interaction, allows a simple semi-classical interpretation as the Coulomb energy of interacting electrons, each distributed in space with the electric charge density $\rho_{nml}(\mathbf{r}) = -e\psi_{nml}^*(\mathbf{r})\psi_{nml}(\mathbf{r})$:¹⁵

$$E_{\text{dir}} = \int d^3r \int d^3r' \frac{\rho_{100}(\mathbf{r})\rho_{nlm}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} = \int \rho_{100}(\mathbf{r})\phi(\mathbf{r})d^3r, \quad (8.46)$$

where $\phi(\mathbf{r})$ is the electrostatic potential created, at point $\mathbf{r}$, by the counterpart electron's “electric charge cloud”:¹⁶

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int d^3r' \frac{\rho_{nlm}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (8.47)$$

However, integral (45b), called the *exchange interaction*, evades a classical interpretation, and (as it is clear from its derivation) is the direct corollary of the electron indistinguishability. The magnitude of E_{ex} is also very much different from E_{dir} , because the function under integral (45b) disappears in those regions where single-particle wavefunctions do not overlap. This is in a full agreement with the discussion in Sec. 1: if two particles are identical but well separated, i.e. their wavefunctions do not overlap, the exchange interaction disappears, because all effects of particle indistinguishability vanish.

Historically, the fact of having two different hydrogen-like spectra (48) and (49) was taken as an evidence for two different species of ^4He , called, respectively, the *orthohelium* and *parahelium*. Figure 1b shows the structure of an excited energy level, with certain quantum numbers $n > 1$, l , and m , given by Eqs. (44)-(45). The upper level, with energy

$$E_{\text{ortho}} = (\epsilon_{100} + \epsilon_{nlm}) + E_{\text{dir}} + E_{\text{ex}} > \epsilon_{100} + \epsilon_{nlm}, \quad (8.48)$$

corresponds to the “orthohelium”, i.e. the symmetric orbital state and hence to the singlet spin state (19), with zero net spin, $s = 0$. The lower level, with

$$E_{\text{para}} = (\epsilon_{100} + \epsilon_{nlm}) + E_{\text{dir}} - E_{\text{ex}} < E_{\text{ortho}}, \quad (8.49)$$

corresponds to “parahelium”, i.e. the antisymmetric orbital, and hence to the triplet spin state(s) with $s = 1$ - see Eq. (21). Its degeneracy may be lifted by magnetic field, so that the splitting is identical to that of an elementary particle with spin $s = 1$. Calculations of the direct and exchange interaction integrals (45) for various values of n and l show that the perturbation theory explains the experimental spectrum of the orthohelium and parahelium (Fig. 1) pretty well.

Encouraged by this success, and motivated by the very important task of description of atoms, molecules, and metals, we may try to apply the same approach to systems with $N > 2$ electrons. In this case the mathematical expression of the Pauli principle for fermions is

¹⁵ See, e.g., EM Sec. 1.3, in particular Eq. (1.54).

¹⁶ Note that the result for E_{dir} correctly reflects the basic fact that a charged particle does not interact with itself, even if its wavefunction is quantum-mechanically spread over a finite space volume. Unfortunately, this is not true for some other approximate theories of multi-particle systems – see Sec. 4 below.

$$\hat{\mathcal{P}}_{kk'} = -1, \quad \text{for all } k, k' = 1, 2, \dots, N, \quad (8.50)$$

where operator $\hat{\mathcal{P}}_{kk'}$ permutes particle with numbers k and k' . In order to understand how common eigenstates of all such operators may be formed, let us return for a minute to two non-interacting electrons, and rewrite Eq. (11) in the following compact form:

$$|\alpha_{-}\rangle = \frac{1}{\sqrt{2}}(|\beta\rangle \otimes |\beta'\rangle - |\beta'\rangle \otimes |\beta\rangle) = \frac{1}{\sqrt{2}} \begin{array}{cc} \text{state 1} & \text{state 2} \\ \downarrow & \downarrow \\ \left| \begin{array}{cc} |\beta\rangle \otimes & |\beta'\rangle \\ \beta\rangle \otimes & \beta'\rangle \end{array} \right\rangle & \begin{array}{l} \leftarrow \text{particle number 1,} \\ \leftarrow \text{particle number 2.} \end{array} \end{array} \quad (8.51)$$

In this way, the Pauli principle is mapped on the well-known property of matrix determinants: if any of two columns of a matrix coincide, its determinant vanishes. This *Slater determinant* approach may be readily generalized to N fermions in N (not necessarily lowest) single-particle states β, β' , etc:

$$|\alpha_{-}\rangle = \frac{1}{(N!)^{1/2}} \left\{ \begin{array}{cccc} \text{state list} \rightarrow & & & \\ \left| \begin{array}{cccc} |\beta\rangle \otimes & |\beta'\rangle \otimes & |\beta''\rangle \otimes & \dots \\ \beta\rangle \otimes & \beta'\rangle \otimes & \beta''\rangle \otimes & \dots \\ \beta\rangle \otimes & \beta'\rangle \otimes & \beta''\rangle \otimes & \dots \\ \dots & \dots & \dots & \dots \end{array} \right\rangle & \begin{array}{l} \text{particle} \\ \text{list} \\ \downarrow \end{array} & N & \\ \underbrace{\hspace{10em}}_N & & & \end{array} \right\} \quad (8.52) \quad \text{Slater determinant}$$

Even though the Slater determinant form is extremely nice and compact (in comparison with direct writing of a sum of $N!$ products, each of N ket factors), there are two major problems with using it for practical calculations:

(i) For the calculation of any bra-ket product (say, within the perturbation theory) we need to spell out each bra- and ket-vector as a sum of component terms. Even for a limited number of electrons (say $N \sim 10^2$ in a typical atom), the number $N! \sim 10^{160}$ of terms in such a sum is impracticably large for any analytical calculation.

(ii) In the case of interacting fermions, Slater determinants do not describe the eigenvectors of the system; rather the stationary state is a *superposition* of such determinants - each for a specific selection of N states from the general set of single-particle states – that is generally different from N .

These challenges make the development of a more general theory that would not use particle numbers (which are superficial for indistinguishable particles to start with) a must for getting any final results for multiparticle systems.

8.3. Second quantization

The most useful formalism for this purpose, that avoids particle numbering at all, is called the *second quantization*.¹⁷ Actually, we have already discussed a particular version of this formalism, for

¹⁷ It was invented (first for photons and then for arbitrary bosons) by P. Dirac in 1927, and then modified in 1928 for fermions by E. Wigner and P. Jordan. The term “second quantization” is rather misleading for the nonrelativistic applications we are discussing, but finds certain justification in the quantum field theory.

the a case of 1D harmonic oscillator's excitations, in Sec. 5.4. As a reminder, we have used Eqs. (5.98) to define the “creation” and “annihilation” operators via the usual operators of coordinate and momentum, and then proved their key property (5.122),

$$\hat{a}^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle, \quad \hat{a} |n\rangle = n^{1/2} |n-1\rangle, \quad (8.53)$$

where n are the stationary (Fock) states of the oscillator. This property allows an interpretation of operators' actions as the creation/annihilation of a single *excitations* of energy $\hbar\omega_0$ - thus justifying the operator names. In the next chapter, we will show that such an excitation of an electromagnetic field mode may be considered as a massless boson with $s = 1$, called the *photon*.

In order to generalize this approach to *arbitrary bosons*, not appealing to a specific system such as the harmonic oscillator, we may use relations similar to Eq. (53) to *define* the creation and annihilation operators. The definition looks simple in the language of the so-called *Dirac states*, with ket-vectors

Dirac
state

$$|N_1, N_2, \dots, N_j, \dots\rangle, \quad (8.54)$$

where N_j are the state *occupancies*, i.e. the numbers of bosons in each single-particle state j . Let me emphasize that here indices $1, 2, \dots, j, \dots$, are the positions of each number in the Dirac ket vector, i.e. are the numbers of single-particle *states* (including their spin parts) rather than *particles*. Thus the very notion of individual particle numbers is completely (and for indistinguishable particles, very relevantly) absent from this formalism. Generally, the set of single-particle states participating in the Dirac state may be selected in an arbitrary way (provided that it is full and orthonormal),

$$\langle N'_1, N'_2, \dots, N'_j, \dots | N_1, N_2, \dots, N_j, \dots \rangle = \delta_{N_1 N'_1} \delta_{N_2 N'_2} \dots \delta_{N_j N'_j} \dots, \quad (8.55)$$

though for system of non- (or weakly) interacting bosons, using the stationary states of individual particles in the system under analysis are almost always the best choice.

Now we can define the *particle annihilation operator* as follows:

Boson
annihilation
operator

$$\hat{a}_j |N_1, N_2, \dots, N_j, \dots\rangle \equiv N_j^{1/2} |N_1, N_2, \dots, N_j - 1, \dots\rangle. \quad (8.56)$$

Note that the pre-ket coefficient, similar to that in Eq. (53), guarantees that an attempt to annihilate a particle in an unpopulated state gives the non-existing (null) state:

$$\hat{a}_j |N_1, N_2, \dots, 0_j, \dots\rangle = 0, \quad (8.57)$$

where symbol 0_j means zero occupancy of j -th state. An alternative way to write Eq. (56) is

$$\langle N'_1, N'_2, \dots, N'_j, \dots | \hat{a}_j |N_1, N_2, \dots, N_j, \dots\rangle = N_j^{1/2} \delta_{N_1 N'_1} \delta_{N_2 N'_2} \dots \delta_{N'_j, N_j - 1} \dots \quad (8.58)$$

According to Eq. (4.65), the matrix element of the Hermitian conjugate operator $\hat{a}_j^\dagger$ is

$$\begin{aligned}
\langle N'_1, N'_2, \dots, N'_j, \dots | \hat{a}_j^\dagger | N_1, N_2, \dots, N_j, \dots \rangle &= \langle N_1, N_2, \dots, N_j, \dots | \hat{a}_j | N'_1, N'_2, \dots, N'_j, \dots \rangle^* \\
&= \langle N_1, N_2, \dots, N_j, \dots | (N'_j)^{1/2} | N'_1, N'_2, \dots, N'_j - 1, \dots \rangle = (N'_j)^{1/2} \delta_{N_1 N'_1} \delta_{N_2 N'_2} \dots \delta_{N_j, N'_j - 1} \dots \\
&= (N_j + 1)^{1/2} \delta_{N_1 N'_1} \delta_{N_2 N'_2} \dots \delta_{N_j + 1, N'_j} \dots,
\end{aligned} \quad (8.59)$$

meaning that

$$\hat{a}_j^\dagger | N_1, N_2, \dots, N_j, \dots \rangle = (N_j + 1)^{1/2} | N_1, N_2, \dots, N_j + 1, \dots \rangle, \quad (8.60)$$

Boson
creation
operator

in the total compliance with the first of Eqs. (53). In particular, this *particle creation operator* $\hat{a}_j^\dagger$ allows the description of the generation of a single particle from the *vacuum* (not null!) state $|0, 0, \dots\rangle$:

$$\hat{a}_j^\dagger | 0, 0, \dots, 0_j, \dots, 0 \rangle = | 0, 0, \dots, 1_j, \dots, 0 \rangle, \quad (8.61)$$

and hence a product of such operators may create, from the vacuum, a multiparticle state with an arbitrary set of occupancies:¹⁸

$$\underbrace{\hat{a}_1^\dagger \hat{a}_1^\dagger \dots \hat{a}_1^\dagger}_{N_1 \text{ times}} \underbrace{\hat{a}_2^\dagger \hat{a}_2^\dagger \dots \hat{a}_2^\dagger}_{N_2 \text{ times}} \dots | 0, 0, \dots \rangle = (N_1! N_2! \dots)^{1/2} | N_1, N_2, \dots \rangle. \quad (8.62)$$

Next, combining Eqs. (56) and (60), we get

$$\hat{a}_j^\dagger \hat{a}_j | N_1, N_2, \dots, N_j, \dots \rangle = N_j | N_1, N_2, \dots, N_j, \dots \rangle, \quad (8.63)$$

so that, just as for the particular case of harmonic oscillator excitations, operator

$$\hat{N}_j \equiv \hat{a}_j^\dagger \hat{a}_j \quad (8.64)$$

Number-
counting
operator

conserves the numbers of particles in all single-particle states, and simultaneously “counts” their number in the j -th state. Acting by the creation-annihilation operators in the reverse order, we get

$$\hat{a}_j \hat{a}_j^\dagger | N_1, N_2, \dots, N_j, \dots \rangle = (N_j + 1) | N_1, N_2, \dots, N_j, \dots \rangle. \quad (8.65)$$

This result shows that for any state of a multiparticle system (which always may be represented as a linear superposition of Dirac states with different sets of N_j), we can write

$$\hat{a}_j \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_j \equiv [\hat{a}_j, \hat{a}_j^\dagger] = \hat{I}, \quad (8.66)$$

again in agreement with what we had for the 1D oscillator – cf. Eq. (5.101). According to Eq. (55), the creation and annihilation operators corresponding to different single-particle states do commute, so that Eq. (66) may be generalized as

Commutation
relations for
bosonic
operators

¹⁸ The resulting Dirac state is *not* an eigenstate of every multiparticle Hamiltonian. However, we will see below that for a set of non-interacting particles it *is* an eigenstate, and thus may be used in the basis for perturbation theories of systems of weakly interacting particles.

$$\boxed{[\hat{a}_j, \hat{a}_{j'}^\dagger] = \hat{I} \delta_{jj'},} \quad (8.67)$$

and that similar bosonic creation and annihilation operators commute, regardless of which states do they act upon:

$$\boxed{[\hat{a}_j^\dagger, \hat{a}_{j'}^\dagger] = [\hat{a}_j, \hat{a}_{j'}] = 0.} \quad (8.68)$$

Relations (66)-(68) are the mathematical expression of the independence of occupancies of different boson states.

As was mentioned earlier, a major challenge in the Dirac approach is to rewrite the Hamiltonian of a multiparticle system, that naturally carries particle numbers k (see, e.g., Eq. (22) for $k = 1, 2$), in the second quantization language, in which there are no these numbers. Let us start with *single-particle* components of such Hamiltonians, i.e. operators of the type

Single-
particle
operator

$$\boxed{\hat{F} = \sum_{k=1}^N \hat{f}_k.} \quad (8.69)$$

where all N operators $\hat{f}_k$ are similar, besides that each of them acts on one specific (k -th) particle, and N is the total number of particles in the system, that is naturally equal to the sum of single-particle state occupancies:

$$N = \sum_j N_j. \quad (8.70)$$

The most important examples of such operators are the kinetic energy of N similar single particles, and their potential energy in an external field:

$$\hat{T} = \sum_{k=1}^N \frac{\hat{p}_k^2}{2m}, \quad \hat{U} = \sum_{k=1}^N \hat{u}(\mathbf{r}_k). \quad (8.71)$$

In order to express a particle-separable operator of the type (69) in terms of the Dirac formalism, we need to return for a minute to the particle-number representations used in the beginning of this chapter. Instead of the Slater determinant (52), for bosons we have to write a similar expression, but without the sign changes (sometimes called the *permanent*):

$$|N_1, \dots, N_j, \dots\rangle = \left(\frac{N_1! \dots N_j! \dots}{N!} \right)^{1/2} \sum_P \left| \underbrace{\dots \beta \beta' \beta'' \dots}_{N \text{ operands}} \right\rangle. \quad (8.72)$$

Note again that the left-hand part of this relation is written in the Dirac notation (that does not use particle numbering), while in its right-hand part, just in relations of Secs. 1-2, particle numbers are coded with the positions of the single-particle states inside the ket-vectors, and the sum is over all different permutations of the states in the ket – cf. Eq. (10). (According to the elementary combinatorics,¹⁹ there are $N!/(N_1! \dots N_j! \dots)$ such permutations, so that the coefficient before the sum ensures the proper normalization of the single-particle states.) Let us use Eq. (72) to spell out the following bra-ket of a system with $(N-1)$ particles:

¹⁹ See, e.g., MA Eq. (2.3).

$$\begin{aligned} & \langle \dots N_j, \dots N_{j'} - 1, \dots | \hat{F} | \dots N_j - 1, \dots N_{j'}, \dots \rangle \\ &= \frac{N_1! \dots (N_j - 1)! \dots (N_{j'} - 1)! \dots}{(N - 1)!} (N_j N_{j'})^{1/2} \sum_{P \langle N-1 |} \sum_{P \langle N-1 |} \langle \dots \beta \beta' \beta'' \dots | \sum_{k=1}^{N-1} \hat{f}_k | \dots \beta \beta' \beta'' \dots \rangle, \end{aligned} \quad (8.73)$$

where all non-specified occupation numbers in the corresponding positions of the bra- and ket-vectors are equal to each other. Each single-particle operator $\hat{f}_k$, participating in the operator sum, acts on the bra- and ket-vectors of states j and j' , respectively, in a certain (say, k^{th}) position, giving the result that does not depend on the position number:

$$\langle \beta_j |_{\text{in } k^{\text{th}} \text{ position}} \hat{f}_k | \beta_{j'} \rangle_{\text{in } k^{\text{th}} \text{ position}} = \langle \beta_j | \hat{f} | \beta_{j'} \rangle \equiv f_{jj'}. \quad (8.74)$$

Since in both permutation sets participating in Eq. (73), with $(N - 1)$ vectors each, all positions are equivalent, we can fix the position (say, take the first one) and replace the sum over k by the multiplication by factor $(N - 1)$. The fraction of permutations with the necessary bra-vector (with number j) in that position is $N_j/(N - 1)$, while that with the necessary ket-vector (with number j') in the same position is $N_{j'}/(N - 1)$. As the result, the permutation sum in Eq. (73) reduces to

$$(N - 1) \frac{N_j}{N - 1} \frac{N_{j'}}{N - 1} f_{jj'} \sum_{P \langle N-2 |} \sum_{P \langle N-2 |} \langle \dots \beta \beta' \beta'' \dots | \dots \beta \beta' \beta'' \dots \rangle, \quad (8.75)$$

where our specific position k is now excluded from both the bra- and ket-vector permutations. Each of these permutations now includes only $(N_j - 1)$ states j and $(N_{j'} - 1)$ states j' , so that, using the state orthonormality, we finally arrive at a very simple result:

$$\begin{aligned} & \langle \dots N_j, \dots N_{j'} - 1, \dots | \hat{F} | \dots N_j - 1, \dots N_{j'}, \dots \rangle \\ &= \frac{N_1! \dots (N_j - 1)! \dots (N_{j'} - 1)! \dots}{(N - 1)!} (N_j N_{j'})^{1/2} (N - 1) \frac{N_j}{N - 1} \frac{N_{j'}}{N - 1} f_{jj'} \frac{(N - 2)!}{N_1! \dots (N_j - 1)! \dots (N_{j'} - 1)! \dots} \\ &= (N_j N_{j'})^{1/2} f_{jj'}. \end{aligned} \quad (8.76)$$

Now let us calculate matrix elements of the following operator:

$$\sum_{j, j'} f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'}. \quad (8.77)$$

A direct application of Eqs. (56) and (60) shows that the only nonvanishing of them are

$$\langle \dots N_j, \dots N_{j'} - 1, \dots | f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'} | \dots N_j - 1, \dots, N_{j'}, \dots \rangle = (N_j N_{j'})^{1/2} f_{jj'}. \quad (8.78)$$

But this is exactly the last form of Eq. (76), so that in the basis of Dirac states, operator (69) may be represented as

$$\hat{F} = \sum_{j, j'} f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'}. \quad (8.79)$$

Single-particle operator: second-quantization form

This beautifully simple equation is the most important formula of the second quantization theory, and is essentially the Dirac-language analog of Eq. (4.59) of the single-particle quantum mechanics. Each term of the sum may be described by a very simple mnemonic rule: if an operator “connects” two

single-particle states j and j' , move the particle from state j' into state j , and weigh the result with the corresponding single-particle matrix element. (One of the corollaries of Eq. (79) is that the expectation value of an operator whose eigenstates coincide with the Dirac states, is

$$\langle F \rangle \equiv \langle \dots N_j, \dots | \hat{F} | \dots N_j, \dots \rangle = \sum_j f_{jj} N_j, \quad (8.80)$$

with an evident physical interpretation as the sum of single-particle expectation values over all states, weighed by state occupancies.)

Proceeding to *fermions*, which have to obey the Pauli principle, we immediately notice that any occupation number N_j may only take two values, 0 or 1. In order to account for that, and also make the key equation (76) valid for fermions as well, the creation-annihilation operators are now defined by relations

$$\hat{a}_j |N_1, N_2, \dots, 0_j, \dots\rangle = 0, \quad \hat{a}_j |N_1, N_2, \dots, 1_j, \dots\rangle = (-1)^{\Sigma(1, j-1)} |N_1, N_2, \dots, 0_j, \dots\rangle, \quad (8.81)$$

$$\hat{a}_j^\dagger |N_1, N_2, \dots, 0_j, \dots\rangle = (-1)^{\Sigma(1, j-1)} |N_1, N_2, \dots, 1_j, \dots\rangle, \quad \hat{a}_j^\dagger |N_1, N_2, \dots, 1_j, \dots\rangle = 0. \quad (8.82)$$

In these relations, symbol $\Sigma(J, J')$ means the sum of all occupancy numbers in state positions from J to J' , including the border points:

$$\Sigma(J, J') \equiv \sum_{j=J}^{J'} N_j, \quad (8.83)$$

so that the sum participating in Eqs. (81) and (82) is the total occupancy of all states with the numbers below j . (The states have to be numbered in a fixed albeit arbitrary order.) As a result, Eqs. (81)-(82) may be readily summarized in the verbal form: if an operator replaces the j^{th} state occupancy with the opposite one (1 with 0, or vice versa), it also changes sign before the result if (and only if) the total number of particles in states with $j' < j$ is odd.

One of corollaries of this (somewhat counter-intuitive) rule of sign alternation is that the sign of the ket-vector of a completely filled two-state system depends on how exactly it has been formed from the vacuum state. Indeed, if we start from creating the fermion in state 1, we get

$$\hat{a}_1^\dagger |0, 0\rangle = (-1)^0 |1, 0\rangle = |1, 0\rangle, \quad \hat{a}_2^\dagger \hat{a}_1^\dagger |0, 0\rangle = \hat{a}_2^\dagger |1, 0\rangle = (-1)^1 |1, 1\rangle = -|1, 1\rangle, \quad (8.84)$$

while if the operator order is different, the result's sign is opposite:

$$\hat{a}_2^\dagger |0, 0\rangle = (-1)^0 |0, 1\rangle = |0, 1\rangle, \quad \hat{a}_1^\dagger \hat{a}_2^\dagger |0, 0\rangle = \hat{a}_1^\dagger |0, 1\rangle = (-1)^0 |1, 1\rangle = +|1, 1\rangle. \quad (8.85)$$

Since the action of any of these operator products on any initial state rather than vacuum gives the null ket, we can write the following operator equality:

$$\hat{a}_1^\dagger \hat{a}_2^\dagger + \hat{a}_2^\dagger \hat{a}_1^\dagger \equiv \{\hat{a}_1^\dagger, \hat{a}_2^\dagger\} = 0. \quad (8.86)$$

It is straightforward to check that this result is valid for the Dirac vector of an arbitrary length, and does not depend on the occupancy of other states, so that we can always write

Fermion
creation-
annihilation
operators

$$\left\{ \hat{a}_j^\dagger, \hat{a}_{j'}^\dagger \right\} = \left\{ \hat{a}_j, \hat{a}_{j'} \right\} = 0; \quad (8.87)$$

these equalities hold for $j = j'$ as well. On the other hand, the absolutely similar calculation shows that the mixed creation-annihilation operator products do depend on whether the states are different or not:²⁰

$$\left\{ \hat{a}_j, \hat{a}_{j'}^\dagger \right\} = \hat{I} \delta_{jj'}. \quad (8.88)$$

Commutation
relations for
fermionic
operators

These equations look very much like Eqs. (67)-(68) for bosons, “only” with the replacement of commutators with anticommutators. Since the core laws of quantum mechanics, including the operator compatibility (Sec. 4.5) and the Heisenberg equation (4.199) of operator evolution in time, involve commutators rather than anticommutators, so that one might think that all the behavior of bosonic and fermionic multiparticle systems should be dramatically different. However, the difference is not as huge as one could expect, for one, a straightforward check shows that the sign factors in Eqs. (81)-(82) compensate those in the Slater determinant, and make the key relation (79) valid for the fermions as well. (Indeed, this is the very goal of the introduction of these factors.)

As the simplest example, let us examine what does the second quantization formalism say about dynamics of non-interacting particles in the system whose single-particle properties we know well, namely two nearly-similar, coupled quantum wells – see Fig. 2.23. If the coupling (tunneling) between the wells is so small that the states localized in the wells are only weakly perturbed, in the basis of these states, the single-particle Hamiltonian of the system may be represented by 2×2 matrix (6.27). Selecting the origin of energy at the middle between energies of unperturbed states, so that coefficient a_0 in Eq. (6.27) vanishes, we can reduce the matrix to

$$\mathbf{h} = \mathbf{a} \cdot \boldsymbol{\sigma} = \begin{pmatrix} a_z & a_- \\ a_+ & -a_z \end{pmatrix}, \quad a_{\pm} \equiv a_x \pm ia_y, \quad (8.89)$$

with eigenvalues

$$\varepsilon_{\pm} = \pm a, \quad a = |\mathbf{a}| = (a_x^2 + a_y^2 + a_z^2)^{1/2}. \quad (8.90)$$

Now following recipe (79), we can represent the Hamiltonian of the whole system of particles in terms of the creation-annihilation operators:

$$\hat{H} = a_z \hat{a}_1^\dagger \hat{a}_1 + a_- \hat{a}_1^\dagger \hat{a}_2 + a_+ \hat{a}_2^\dagger \hat{a}_1 - a_z \hat{a}_2^\dagger \hat{a}_2, \quad (8.91)$$

where $\hat{a}_{1,2}^\dagger$ and $\hat{a}_{1,2}$ are the operators of creation and annihilation of a particle localized in the corresponding quantum well. According to Eq. (64), the first and the last terms of the right-hand part of Eq. (91) describe particle energies in uncoupled wells,

$$a_z \hat{a}_1^\dagger \hat{a}_1 = \varepsilon_1 \hat{N}_1, \quad -a_z \hat{a}_2^\dagger \hat{a}_2 = \varepsilon_2 \hat{N}_2, \quad (8.92)$$

²⁰ A by-product of this calculation is a proof that operator (57) counts the number of particles N_j (now equal to either 1 or 0), just as it does for bosons.

while the sum of middle two terms is the second-quantization description of tunneling between the wells.

Now we can use the general Eq. (4.199) of the Heisenberg picture to find the equations of motion for the creation-annihilation operators. For example,

$$i\hbar\dot{\hat{a}}_1 = [\hat{a}_1, \hat{H}] = a_z [\hat{a}_1, \hat{a}_1^\dagger \hat{a}_1] + a_- [\hat{a}_1, \hat{a}_1^\dagger \hat{a}_2] + a_+ [\hat{a}_1, \hat{a}_2^\dagger \hat{a}_1] - a_z [\hat{a}_1, \hat{a}_2^\dagger \hat{a}_2]. \quad (8.93)$$

Since the Bose and Fermi operators satisfy different commutation relations, one could expect the right hand part of this equation would be different for bosons and fermions. However, it is not so. Indeed, all commutators in the right-hand part of Eq. (93) have the following form:

$$[\hat{a}_j, \hat{a}_{j'}^\dagger \hat{a}_{j''}] \equiv \hat{a}_j \hat{a}_{j'}^\dagger \hat{a}_{j''} - \hat{a}_{j'}^\dagger \hat{a}_{j''} \hat{a}_j. \quad (8.94)$$

According to Eqs. (67) and (88), the first pair product of the operators may be recast as

$$\hat{a}_j \hat{a}_{j'}^\dagger = \hat{I} \delta_{jj'} \pm \hat{a}_{j'}^\dagger \hat{a}_j, \quad (8.95)$$

where the upper sign pertains to bosons and the lower to fermions, while according to Eqs. (68) and (87), the very last pair product is

$$\hat{a}_{j''} \hat{a}_j = \pm \hat{a}_j \hat{a}_{j''}, \quad (8.96)$$

with the same sign convention. Plugging these expressions into Eq. (94), we see that regardless of the particle statistics, two last terms cancel, and we arrive at a universal (and generally very useful) commutation rule

$$[\hat{a}_j, \hat{a}_{j'}^\dagger \hat{a}_{j''}] = \hat{a}_{j''} \delta_{jj'}, \quad (8.97)$$

valid for particles of both kinds. As a result, the Heisenberg equation of motion for operator $\hat{a}_1$, and the equation for $\hat{a}_2$ (that may be obtained absolutely similarly), are also statistics-independent:²¹

$$\begin{aligned} i\hbar\dot{\hat{a}}_1 &= a_z \hat{a}_1 + a_- \hat{a}_2, \\ i\hbar\dot{\hat{a}}_2 &= a_+ \hat{a}_1 - a_z \hat{a}_2. \end{aligned} \quad (8.98)$$

Thus we have got a system of coupled, linear differential equations that are identical to equations for the c -number probability amplitudes of single-particle wavefunctions of a two-level system – see Eq. (2.201) and Problem 4.10. Their general solution is a linear superposition of exponents:

$$\hat{a}_{1,2}(t) = \sum_{\pm} \hat{c}_{1,2}^{(\pm)} \exp\{\lambda_{\pm} t\}. \quad (8.99)$$

²¹ Equations of motion for creation operators $\hat{a}_{1,2}^\dagger$ are just the Hermitian-conjugates of Eqs. (98), and do not add any new information about system's dynamics.

As usual, in order to find exponents $\lambda_{\pm}$, it is sufficient to plug in a particular solution $\hat{a}_{1,2}(t) = \hat{c}_{1,2} \exp\{\lambda t\}$ into Eq. (98) and require that the determinant of the resulting homogeneous, linear system for “coefficients” (actually, time-independent operators) $\hat{c}_{1,2}$ equals zero. This gives us the following characteristic equation

$$\begin{vmatrix} a_z - i\hbar\lambda & a_- \\ a_+ & -a_z - i\hbar\lambda \end{vmatrix} = 0, \quad (8.100)$$

with two roots $\lambda_{\pm} = \pm i\Omega/2$, where $\Omega \equiv 2a/\hbar$. Now plugging each of the roots, one by one, into the system of equations for $\hat{c}_{1,2}$, we can find these operators, and hence the general solution of system (98) for arbitrary initial conditions.

Let us consider the simple case $a_y = a_z = 0$ (meaning in particular that the well eigenenergies are exactly aligned), so that $\hbar\Omega/2 \equiv a = a_x$; then the solution of Eq. (98) is

$$\hat{a}_1(t) = \hat{a}_1(0) \cos \frac{\Omega t}{2} - i\hat{a}_2(0) \sin \frac{\Omega t}{2}, \quad \hat{a}_2(t) = -i\hat{a}_1(0) \sin \frac{\Omega t}{2} + \hat{a}_2(0) \cos \frac{\Omega t}{2}. \quad (8.101)$$

Multiplying the first of Eqs. (101) by its Hermitian conjugate, and ensemble-averaging the result, we get

$$\begin{aligned} \langle N_1 \rangle = \langle \hat{a}_1^\dagger(t) \hat{a}_1(t) \rangle &= \langle \hat{a}_1^\dagger(0) \hat{a}_1(0) \rangle \cos^2 \frac{\Omega t}{2} + \langle \hat{a}_2^\dagger(0) \hat{a}_2(0) \rangle \sin^2 \frac{\Omega t}{2} \\ &\quad - i \langle \hat{a}_1^\dagger(0) \hat{a}_2(0) + \hat{a}_2^\dagger(0) \hat{a}_1(0) \rangle \sin \frac{\Omega t}{2} \cos \frac{\Omega t}{2}. \end{aligned} \quad (8.102)$$

Quantum oscillations:
second quantization form

Let us consider the particular case when the initial state of the system is a Dirac state, i.e. has a definite number of particles in each well; in this case only two first terms in the right hand part are different from zero:²²

$$\langle N_1 \rangle = N_1(0) \cos^2 \frac{\Omega t}{2} + N_2(0) \sin^2 \frac{\Omega t}{2}. \quad (8.103)$$

For one particle, initially placed in either well, this gives us our old result (2.185) describing quantum oscillations of the particle between two wells with frequency Ω . However, Eq. (103) is valid for any set of initial occupancies; let us use it. For example, starting from two particles, with initially one particle in each well, we get $\langle N_1 \rangle = 1$, regardless of time. So, the occupancies do not oscillate, and no experiment may detect the quantum oscillations, though their frequency Ω is still formally present in the time evolution equations. This fact may be interpreted as the simultaneous quantum oscillations of two particles exactly in anti-phase. For bosons, we can go to even larger occupancies by preparing the system, for example, in the state with $N_1(0) = N$, $N_2(0) = 0$. Equation (103) says that in this case we see that the quantum oscillation amplitude increases N -fold; this is a particular manifestation of the general fact that bosons can be (and evolve in time) in the same quantum state. On the other hand, for fermions we cannot increase initial occupancies beyond 1, so that the largest oscillation amplitude we can get is if we initially fill just one well.

²² For the second well's occupancy, the result is complementary, $N_2(t) = N_1(0) \sin^2 \Omega t + N_2(0) \cos^2 \Omega t$, giving in particular a good sanity check: $N_1(t) + N_2(t) = N_1(0) + N_2(0) = \text{const}$.

The Dirac approach may be readily generalized to more complex systems. For example, an arbitrary system of quantum wells with weak tunneling coupling between the adjacent wells may be described by Hamiltonian

$$\hat{H} = \sum_j \varepsilon_j a_j^\dagger \hat{a}_j + \sum_{\langle j,j' \rangle} \delta_{jj'} a_j^\dagger \hat{a}_{j'} + \text{h.c.}, \quad (8.104)$$

where symbol $\langle j,j' \rangle$ means that the second sum is restricted to pairs of next-neighbor wells – see, e.g., Eq. (2.203) and its discussion. Note that this Hamiltonian is still a quadratic form of the creation-annihilation operators, so the Heisenberg-picture equations of motion of these operators are linear, and its exact solutions, though possibly cumbersome, may be studied in detail. Due to this fact, Hamiltonian (104) is widely used for the study of some phenomena, for example the very interesting *Anderson localization* effect, in which a random distribution of eigenenergies ε_j prevents particles within certain energy range from spreading to unlimited distances.^{23,24}

8.4. Perturbative approaches

The situation becomes much more difficult if the problem requires an account of direct interactions between the particles. Let us assume that the interaction may be reduced to that between pairs – as it is the case at their Coulomb interaction²⁵ and most other interactions, so that it may be described with the following “pair-interaction” Hamiltonian

$$\hat{U}_{\text{int}} = \frac{1}{2} \sum_{\substack{k,k'=1 \\ k \neq k'}}^N \hat{u}_{\text{int}}(\mathbf{r}_k, \mathbf{r}_{k'}), \quad (8.105)$$

Pair-
interaction
Hamiltonian
in two
alternative
forms

with the front factor of $1/2$ compensating the double-counting of each particle pair. The translation of this operator to the second-quantization form may be done absolutely similarly to the derivation of Eq. (77), and gives a similar (though naturally more bulky) result²⁶

$$\hat{U}_{\text{int}} = \frac{1}{2} \sum_{j,j',l,l'} u_{jj' ll'} \hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_{l'} \hat{a}_l, \quad (8.106)$$

where the two-particle matrix elements are defined similarly to Eq. (74):

$$u_{jj' ll'} \equiv \langle \beta_j \beta_{j'} | \hat{u}_{\text{int}} | \beta_l \beta_{l'} \rangle. \quad (8.107)$$

Even in this case, the resulting Heisenberg equations of motion are nonlinear, so that solving them and calculating observables from the results is usually impossible, at least analytically. The only

²³ For a review of the 1D version of this problem, see, e.g., J. Pendry, *Adv. Phys.* **43**, 461 (1994).

²⁴ To complete this section, I have to note, at least in passing, a different form of the second-quantization formalism, based on the so-called *field operators*. It will be more natural for me to discuss it in the next chapter.

²⁵ Another important example is the so-called *Hubbard model* in which there may be only two particles on each of localized sites, with the negligible interaction of particles on different sites – which are only connected by the next-neighbor tunneling – see Eq. (104).

²⁶ The only new feature is a specific order of the indices of the creation operators. Note the mnemonic rule of writing this expression, similar to that for Eq. (79): each term corresponds to moving a pair of particles from states l and l' to states j' and j , factored with the corresponding two-particle matrix element (107).

case when some general results may be obtained is the weak interaction limit. In this case the unperturbed Hamiltonian contains only single-particle terms such as in Eqs. (71), so we can always (at least conceptually :-)) find such a basis of orthonormal single-particle states β_j in which that Hamiltonian is diagonal in the Dirac representation:

$$\hat{H}^{(0)} = \sum_j \varepsilon_j^{(0)} \hat{a}_j^\dagger \hat{a}_j. \quad (8.108)$$

Now we can use Eq. (6.13) in this basis to calculate the interaction energy as a first-order perturbation:

$$\begin{aligned} E_{\text{int}}^{(1)} &= \langle N_1, N_2, \dots | \hat{U}_{\text{int}} | N_1, N_2, \dots \rangle = \frac{1}{2} \langle N_1, N_2, \dots | \sum_{j,j',l,l'} u_{jj' ll'} \hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_l \hat{a}_{l'} | N_1, N_2, \dots \rangle \\ &= \frac{1}{2} \sum_{j,j',l,l'} u_{jj' ll'} \langle N_1, N_2, \dots | \hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_l \hat{a}_{l'} | N_1, N_2, \dots \rangle. \end{aligned} \quad (8.109)$$

Since, according to Eqs. (81)-(82), the Dirac states with different occupancies are orthogonal, the last average yields nonvanishing results only for three particular subsets of the indices:

(i) $j \neq j'$, $l = j$, and $l' = j'$. In this case the 4-operator product in Eq. (109) equals $\hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_j \hat{a}_{j'}$, and applying the commutation rules twice, we can bring it to the so-called *normal ordering*, with each creation operator standing to the right of the corresponding annihilation operator, thus forming the particle number operator (64):

$$\hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_j \hat{a}_{j'} = \pm \hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_{j'} \hat{a}_{j'} = \pm \hat{a}_j^\dagger \left(\pm \hat{a}_j \hat{a}_{j'}^\dagger \right) \hat{a}_{j'} = \hat{a}_j^\dagger \hat{a}_j \hat{a}_{j'}^\dagger \hat{a}_{j'} = \hat{N}_j \hat{N}_{j'}, \quad (8.110)$$

with the similar sign of the final result for bosons and fermions.

(ii) $j \neq j'$, $l = j'$, and $l' = j$. In this case the 4-operator product equals $\hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_{j'} \hat{a}_j$, and bringing it to the form $\hat{N}_j \hat{N}_{j'}$ requires only one commutation:

$$\hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_{j'} \hat{a}_j = \hat{a}_j^\dagger \left(\pm \hat{a}_j \hat{a}_{j'}^\dagger \right) \hat{a}_{j'} = \pm \hat{a}_j^\dagger \hat{a}_j \hat{a}_{j'}^\dagger \hat{a}_{j'} = \pm \hat{N}_j \hat{N}_{j'}, \quad (8.111)$$

with the upper sign for bosons and lower sign for fermions.

(iii) All indices equal to each other, giving $\hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_j = \hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_j$. For fermions, such operator (that “tries” to create or kill two particles in a row, in the same state) immediately gives the null vector. In the case of bosons, we may use Eq. (66) to commute the internal pair of operators, getting

$$\hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_j = \hat{a}_j^\dagger \left(\hat{a}_j \hat{a}_j^\dagger - \hat{I} \right) \hat{a}_j = \hat{N}_j (\hat{N}_j - \hat{I}). \quad (8.112)$$

Note, however, that this formula formally covers the fermion case as well (always giving zero). As a result, Eq. (109) may be rewritten in the following universal form:

$$E_{\text{int}}^{(1)} = \frac{1}{2} \sum_{\substack{j,j' \\ j \neq j'}} N_j N_{j'} (u_{jj' jj'} \pm u_{jj' jj}) + \frac{1}{2} \sum_j N_j (N_j - 1) \dots u_{jjjj}. \quad (8.113)$$

Particle
interaction:
1st-order
energy
perturbation

The consequences of this result are very different for bosons and fermions. In the former case, the last term usually dominates, because the matrix elements (107) are typically the largest when all basis functions coincide. Note that this term allows a very simple interpretation: the number of the diagonal matrix elements it sums up for each state (j) is just the number of interacting particle pairs residing in that state.

In contrast, for fermions the last term is zero, and the interaction energy is the difference of two terms inside the first parentheses. In order to spell them out, let us consider the case when there is no direct spin-orbit interaction. Then vectors $|\beta_j\rangle$ of the single-particle state basis may be represented as products $|o\rangle_j \otimes |m\rangle_j$ of their orbital and spin orientation parts. (Here, for brevity, I am using m instead of m_s .) For spin- $1/2$ particles (say, electrons), these orientations m may equal only $+1/2$ and $-1/2$; in this case the spin part of bra-ket $u_{jj'j'}$ equals

$$\langle m | \otimes \langle m' | m' \rangle \otimes | m' \rangle, \quad (8.114)$$

where, as in the general Eq. (107), the position of a particular vector in a product codes the particle number. Now since spins of different electrons are defined in different Hilbert spaces, we may move their vectors around to get

$$\langle m | \otimes \langle m' | m \rangle \otimes | m' \rangle = (\langle m | m \rangle)_1 \times (\langle m' | m' \rangle)_2 = 1, \quad (8.115)$$

for any pair of j and j' . On the other hand, $u_{jj'j'}$ is proportional to

$$\langle m | \otimes \langle m' | m' \rangle \otimes | m \rangle = (\langle m | m' \rangle)_1 \times (\langle m' | m \rangle)_2 = \delta_{mm'}. \quad (8.116)$$

In this case, it is convenient to rewrite Eq. (113) in the coordinate representation, using single-particle wavefunctions called *spin-orbitals*

Spin-orbital functions

$$\psi_j(\mathbf{r}) \equiv \langle \mathbf{r} | \beta_j \rangle = \langle \mathbf{r} | o_j \rangle \otimes | m \rangle_j. \quad (8.117)$$

They differ from the “usual” orbital wavefunctions of the type (5.19) only by that their index j should be understood as the set of the orbital state index and the spin orientation index m .²⁷ Also, due to the Pauli-principle restriction of numbers N_j to either 0 or 1, Eq. (113) may be also rewritten without the occupancy numbers, with the understanding that the summation is extended only over the pairs of occupied states. As a result, Eq. (113) becomes

Energy correction due to fermion interaction

$$E_{\text{int}}^{(1)} = \frac{1}{2} \sum_{\substack{j, j' \\ j \neq j'}} \int d^3 r \int d^3 r' \left[\begin{aligned} &\psi_j^*(\mathbf{r}) \psi_{j'}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_j(\mathbf{r}) \psi_{j'}(\mathbf{r}') \\ &- \psi_j^*(\mathbf{r}) \psi_{j'}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_{j'}(\mathbf{r}) \psi_j(\mathbf{r}') \end{aligned} \right]. \quad (8.118)$$

If, for a system of 2 electrons, we limit the summation to 2 states ($j, j' = 1, 2$), we get the result absolutely similar to Eqs. (44)-(45), with the minus sign in Eq. (44). Hence, Eq. (118) may be considered as the generalization of the direct and exchange interaction balance picture to an arbitrary number of orbitals and an arbitrary total number N of electrons. Note, however, that this equation cannot

²⁷ Constructs (117) are also close to spinors (14), besides that the spin s of a single particle is fixed, so that the spin-orbital should be indexed by spin's orientation $m \equiv m_s$ rather than the full spin s . Also, the orbital index should be clearly distinguished from j (which, again, is the set of that orbital index *and* m). This is why I believe that the frequently met notation of spinors as $\psi_{j,s}(\mathbf{r})$ may lead to confusion.

correctly describe the energy of the excited singlet state, corresponding to the plus sign in Eq. (44).²⁸ The reason is that the description of entangled spin states, given by Eq. (19) and the last term of Eq. (21), require *linear superpositions* of different Dirac states, and hence not covered by our assumption (108).

Now comes a very important fact: the *approximate* result (118), added to the sum of unperturbed energies $\varepsilon_j^{(0)}$, equals the sum of *exact* eigenenergies of the so-called *Hartree-Fock equation*:²⁹

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + u(\mathbf{r}) \right) \psi_j(\mathbf{r}) + \sum_{j' \neq j} \int \left[\psi_{j'}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_j(\mathbf{r}) \psi_{j'}(\mathbf{r}') - \psi_{j'}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_{j'}(\mathbf{r}) \psi_j(\mathbf{r}) \right] d^3 r' = \varepsilon_j \psi_j(\mathbf{r}), \quad (8.119)$$

Hartree-Fock equation

where $u(\mathbf{r})$ is the external-field potential acting on each particle separately – see Eq. (71). An advantage of this equation in comparison with Eq. (118) is that it allows the (approximate) calculation of not only the energy of the system, but also the corresponding spin-orbitals, taking into account the electron-electron interaction.

In the limit when the single-particle wavefunction overlaps are small and hence the exchange interaction is negligible, the last term in square brackets may be ignored, term $\psi_j(\mathbf{r})$ may be taken out of the integral, and becomes similar to the single-particle Schrödinger equation with the following effective potential

$$u_{\text{ef}}(\mathbf{r}) = u(\mathbf{r}) + u_{\text{dir}}(\mathbf{r}), \quad u_{\text{dir}}(\mathbf{r}) = \sum_{j' \neq j} \int \psi_{j'}^*(\mathbf{r}') u_{\text{int}}(\mathbf{r}, \mathbf{r}') \psi_{j'}(\mathbf{r}') d^3 r'. \quad (8.120)$$

Hartree approximation

This is the so-called *Hartree approximation* – that gives reasonable results for some systems.³⁰ However, in dense electrons systems (such as typical atoms, molecules, and condensed matter) the exchange interaction, described by the second term in the square brackets of Eq. (119), is typically of the order of 30% of the direct interaction, and frequently this effect cannot be ignored. In this case, Eq. (119) is an *integro-differential* rather than just differential equation.

There are efficient methods of numerical solution of such equations, typically based on iterative methods, though they require large memory and CPU-cycle resources even for systems of $\sim 10^2$ electrons.³¹ This is why the Hartree-Fock approximation is the de-facto baseline of all so-called *ab-initio*

²⁸ Note that due to condition $j' \neq j$, and Eq. (116), the exchange interaction is limited to electron state pairs with the same spin direction – again in a good correspondence with the triplet states (like $\uparrow\uparrow$ or $\downarrow\downarrow$) of a two-electron system, in which the contribution of E_{ex} (8.45b) to the total energy is also negative.

²⁹ This equation was suggested in 1929 by D. Hartree for the direct interaction, and extended to the exchange interaction by V. Fock in 1930. In order to verify its equivalence to Eq. (118), it is sufficient to multiply all terms of Eq. (119) by $\psi_j^*(\mathbf{r})$, integrate them over all $\mathbf{r}$ space (so that the right-hand part would give ε_j), and then sum these single-particle energies over all occupied states j .

³⁰ An extreme expression of the Hartree approximation is the very simple *Thomas-Fermi model* of heavy atoms (with the atomic number $Z \gg 1$), in which the gradient of the electrostatic potential is also neglected, i.e. the atomic electrons are treated essentially as an ideal Fermi gas – see SM Chapter 3.

³¹ Surprisingly, this is sufficient to describe, with reasonable accuracy, many properties of condensed matter, by breaking it to similar elementary spatial cells (say, Bravais cells of crystals), with cyclic boundary conditions and a limited number of electrons in each cell.

(“first-principle”) calculations in condensed matter physics and quantum chemistry.³² In departures from this baseline, there are two opposite trends. For larger accuracy (and typically smaller systems), several “post-Hartree-Fock methods”, notably including the *configuration interaction* method,³³ that are more complex but may provide higher accuracy, have been developed.

There is also a strong opposite trend of extending *ab-initio* methods to larger systems, while sacrificing the result accuracy and reliability. This trend is currently dominated by the *Density Functional Theory*,³⁴ universally known by its acronym DFT. In this approach, the equation solved for each eigenfunction $\psi_j(\mathbf{r})$ is a differential, Schrödinger-like *Kohn-Sham equation*

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + u(\mathbf{r}) + u_{\text{dir}}^{\text{KS}}(\mathbf{r}) - u_{\text{XC}}(\mathbf{r}) \right] \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}), \quad (8.121)$$

where

$$u_{\text{dir}}^{\text{KS}}(\mathbf{r}) = -e\phi(\mathbf{r}), \quad \phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad \rho(\mathbf{r}) = -en(\mathbf{r}), \quad (8.122)$$

and $n(\mathbf{r})$ is the total electron density in a particular point, calculated as

$$n(\mathbf{r}) \equiv \sum_j \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}). \quad (8.123)$$

The effective *exchange-correlation* potential $u_{\text{XC}}(\mathbf{r})$ (that differs from the genuine exchange potential, participating in Eq. (121), by the inclusion of the term with $j = j'$) is calculated in various approximations, most valid only asymptotically in the limit when the electron number is high. The simplest of them is the *Local Density Approximation* (LDA) in which the effective exchange potential at each point is a function only of the electron density (123) at the same point, taken from the theory of a *uniform* gas of free electrons.³⁵ Another simplification, that dramatically cuts the computing resources necessary for systems of relatively heavy atoms, is the exclusion of the filled internal electron shells (see Sec. 3.7) from the explicit calculations, because the shell states are virtually unperturbed by the valence electron effects involved in typical atomic phenomena and chemical reactions. In this approach, the Coulomb field of the shells, described by fixed, pre-calculated and tabulated *pseudo-potentials*, added to that of the nuclei. Unfortunately, because of lack of time, for details I have to refer the reader to specialized literature.³⁶

³² See, e.g., A. Szabo and N. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill, 1989.

³³ That method, in particular, allows the calculation of proper linear superpositions of the Dirac states (such as the excited singlet state for $N = 2$, discussed above) which are missing in the generic Hartree-Fock approach.

³⁴ It was developed by W. Kohn and coauthors in the mid-1960s, and eventually (in 1998) awarded with a Nobel prize in chemistry.

³⁵ For a uniform, degenerate Fermi-gas of electrons (with the Fermi energy $\varepsilon_F \gg k_B T$), the exchange potential may be calculated analytically, giving $u_{\text{ex}} = (3/4\pi)e^2 k_F / 4\pi\epsilon_0$, where k_F is the Fermi-surface wave number that defines both the Fermi energy $\varepsilon_F = (\hbar k_F)^2 / 2m$ and the electron density (per unit volume) $n = 2(4\pi/3)k_F^3 / (2\pi)^3 \equiv k_F^3 / 3\pi^2$.

³⁶ See, e.g., G. te Velde *et al.*, *J. Comp. Chem.* **22**, 931 (2001), and/or M. D. Segall *et al.*, *J. Phys. – Cond. Matt.* **14**, 2717 (2002), and references therein.

Let me, however, emphasize that despite the wide use of the DFT,³⁷ and its undisputable successes in describing some experimental data, it has problems. For me personally, its largest conceptual deficiency is the incorporation of the absolutely unphysical Coulomb interaction of an electron with itself (by dropping condition $j' \neq j$). As a result, existing DFT packages require substantial artificial tinkering to use them for description of such processes as single-electron transfer.³⁸ A little bit light-heartedly (but still correctly), one may say that an advanced DFT software package, run on a huge supercomputer, cannot be used to calculate the correct energy spectrum of a hydrogen atom – a century after this had been done by Niels Bohr on a slip of paper!

8.5. Quantum computation and cryptography

Now I have to review the emerging fields of *quantum computation* and *encryption*.³⁹ These fields are currently the subject of a very intensive research effort, which has brought (besides much hype :-) a few results of genuine importance for quantum mechanics. My coverage, by necessity short, will emphasize these fundamental results, referring the reader interested in details to special literature.⁴⁰ Because of the active stage of the fields, I will also provide quite a few references to recent publications, making the style of this section closer to a brief research review than to a part of a textbook.

Presently, the work on quantum computation and encryption is focused on systems of spatially-separated (and hence *distinguishable*) two-level systems - in this context, commonly called *qubits*.⁴¹ Due to this distinguishability, the issues that were the focus of the past few sections (including the benefits of the second quantization) are irrelevant here. On the other hand, systems of distinguishable qubits have some interesting properties that had not been yet discussed in this course.

First of all, a system of $N \gg 1$ qubits may contain much more information than the N classical bits – which is the maximum information capacity of N classical bistable systems. Indeed, according to the discussions in Chapter 4, an arbitrary pure state of a single qubit may be represented by its ket vector (4.37) – see also Eq. (5.1):

$$|\alpha\rangle_{N=1} = \alpha_1 |u_1\rangle + \alpha_2 |u_2\rangle, \quad (8.124)$$

where $\{u\}$ is any orthonormal two-state basis. In the quantum information theory, it is natural and common to employ, as u_j , the eigenstates a_j of the observable A that is eventually measured in the particular physical implementation of the qubit - say, a certain spatial component of spin- $1/2$ particle, etc. It is also common to write the kets of these base states as $|0\rangle$ and $|1\rangle$, so that Eq. (124) takes the form⁴²

³⁷ This popularity is enhanced by the availability of several advanced DFT software packages, some of them (such as SIESTA, <http://icmab.cat/leem/siesta/>) in public domain.

³⁸ See, e.g., N. Simonian *et al.*, *J. Appl. Phys.* **113**, 044504 (2013).

³⁹ Since these fields are much related, they are often referred to together, under the (somewhat misleading) title of “quantum information”.

⁴⁰ Despite many recent book titles in the field, one of its first surveys, by M. Nielsen and I. Chuang, *Quantum Computation and Quantum Information*, Cambridge U. Press, 2000, is perhaps still the best one.

⁴¹ In some texts, the term qubit (or “Qbit”, or “Q-bit”) is used instead for the *information contents* of a two-level system – very much like the classical bit of information (in this context, frequently called “Cbit” or “C-bit”) describes the information contents of a classical bistable system – see, e.g., SM Sec. 2.2.

⁴² The slightly odd aspect of this notation is that at the Bloch sphere representation (Fig. 5.1), the North Pole state (that is traditionally denoted as $\uparrow$ in other fields of quantum mechanics) is taken for 0, while the South Pole state $\downarrow$ for 1, so that Eqs. (5.4) take the form $a_0 = \cos(\theta/2)$, $a_1 = \sin(\theta/2)\exp\{i\varphi\}$.

Single qubit
state's
representation

$$|\alpha\rangle_{N=1} = a_0|0\rangle + a_1|1\rangle = \sum_{j=0,1} a_j |j\rangle, \quad (8.125)$$

where in the rest of this chapter, letter j will be used to denote an integer equal to either 0 or 1. Hence any pure state α of a qubit is completely defined by two complex c -numbers a_j , i.e. by 4 real numbers. Moreover, due to the normalization condition $|a_0|^2 + |a_1|^2 = 1$, we need just 3 independent real numbers – say, the Bloch sphere coordinates θ and φ (see Fig. 5.1), plus the common phase γ , which becomes important when we consider coherent states of several qubits – see Eq. (5.3).

Now, if we have a system of 2 qubits, its arbitrary pure state (4.37) may be represented as a sum of $2^2 = 4$ terms,⁴³

Two-qubit
state's
representation

$$|\alpha\rangle_{N=2} = a_{00}|00\rangle + a_{01}|01\rangle + a_{10}|10\rangle + a_{11}|11\rangle \equiv \sum_{j_1, j_2=0,1} a_{j_1 j_2} |j_1 j_2\rangle, \quad (8.126)$$

with 4 complex coefficients, i.e. $4 \times 2 = 8$ real numbers, subject to just one normalization condition⁴⁴

$$\sum_{j_1, j_2=0,1} |a_{j_1 j_2}|^2 = 1. \quad (8.127)$$

An evident generalization of Eqs. (125)-(126) to an arbitrary pure state of an N -qubit system is given by a sum of 2^N terms:

$$|\alpha\rangle_N = \sum_{j_1, j_2, \dots, j_N=0,1} a_{j_1 j_2 \dots j_N} |j_1 j_2 \dots j_N\rangle, \quad (8.128)$$

including all possible combinations of 0s and 1s inside the ket, so that the state is fully described by 2^N complex numbers, i.e. $2 \cdot 2^N = 2^{N+1}$ real numbers, with only one constraint, similar to Eq. (127), imposed by the normalization condition. Let me emphasize that this exponential growth of the information contents would not be possible without the qubit state entanglement. Indeed, in the particular case when qubit states are unentangled (separable),

$$|\alpha\rangle_N = |\alpha_1\rangle |\alpha_2\rangle \dots |\alpha_N\rangle, \quad (8.129)$$

where each $|\alpha_n\rangle$ is described by an equality similar to Eq. (125) with its individual expansion coefficients, the system state description requires only $3N$ real numbers - e.g., N sets $\{\theta, \varphi, \gamma\}$.

However, it is wrong (as it is sometimes done in popular reviews) to project this exponential growth of information contents directly on the capabilities of quantum computation, because this process has to include the output information readout, i.e. qubit state measurements. Due to the fundamental intrinsic uncertainty of quantum systems, the measurement of a single qubit even in a pure state (125) generally gives uncertain results, with probabilities $W_0 = |a_0|^2$ and $W_1 = |a_1|^2$. In order to comply with the general notion of digital computation, a quantum computer has to provide certain (or

⁴³ Here and in most instances below I use the same shorthand notation as was used in the beginning of this chapter – cf. Eq. (8.1). In this short form, qubit's number is coded by the order of its state index inside the single ket-vector, while in the long form, such as in Eq. (129), it is coded by the order of the ket-vector.

⁴⁴ It follows from the requirement that the sum of two probabilities $W_j = \langle \alpha | \hat{P}_j | \alpha \rangle$ (where $\hat{P}_j = |j\rangle\langle j|$ is the corresponding projection operator, see Sec. 4.5) to find one of qubits in one of its two possible states j , equals 1. It is remarkable that the application of this condition to *any* of the qubits results in the same Eq. (127).

virtually certain) results, and hence probabilities W_j have to be very close to either 0 or 1, so that before the measurement, each qubit has to be in a basis state - either 0 or 1. This means that the computational system of N qubits, just before the final readout, has to be one of the basis states

$$|\alpha\rangle_N = |j_1\rangle|j_2\rangle\cdots|j_N\rangle \equiv |j_1j_2\cdots j_N\rangle, \quad (8.130)$$

which is a very small subset even of the set (129) of all unentangled states, and whose maximum information contents in just N classical bits.

Now the reader may start thinking that this constraint strips quantum computations of any advantages over their classical counterparts, but this view is also superficial. In order to show that, let us consider the scheme of the most frequently explored type of quantum computation, shown in Fig. 2.⁴⁵

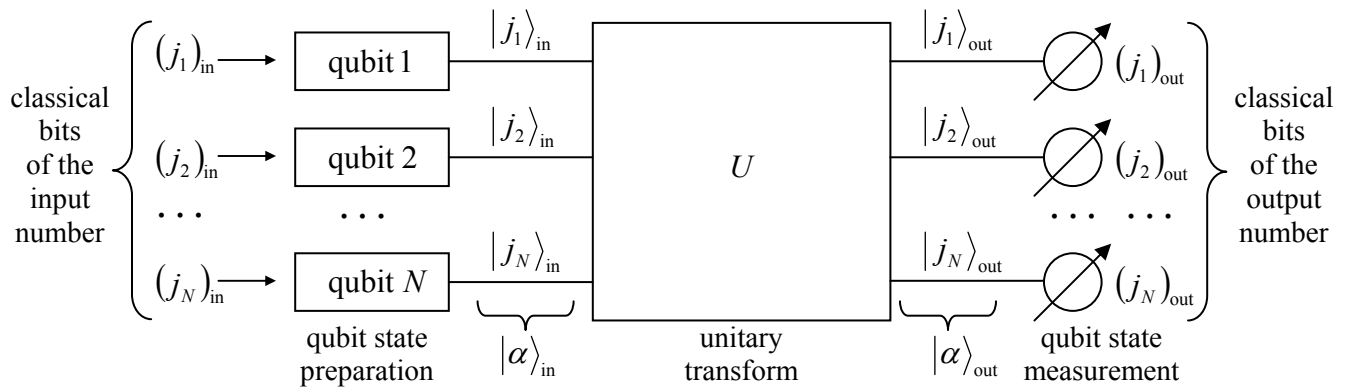


Fig. 8.2. The baseline scheme of quantum computation.

Here each horizontal line (sometimes called a “wire”⁴⁶) corresponds to a single qubit, tracing its time evolution in the same direction as at the usual time function plots: from left to right. This means that the left column $|\alpha\rangle_{\text{in}}$ of ket-vectors describes the initial state of qubits,⁴⁷ while the right column $|\alpha\rangle_{\text{out}}$ describes their final (pre-detector) state. The box labeled U represents the qubit evolution in time due to

⁴⁵ Numerous modifications of this baseline scheme have been suggested, for example with the number of output qubits different from that of input qubits, etc. Some other options are discussed in the end of this section.

⁴⁶ The notion of “wires” stems from the similarity between these diagrams and the drawings used to describe classical computation circuits (see, e.g., Fig. 3a below); in the latter case the lines may be indeed understood as physical wires connecting physical devices: logic gates and/or memory cells. In this context note that classical computer components also have nonvanishing time delays, so that even in this case the left-to-right device ordering is useful to indicate the timing of (and frequently the causal relation between) the signals.

⁴⁷ As we know from Chapter 7, the preparation of pure state (125) is (conceptually :-) straightforward. Placing a qubit into a weak contact with an environment of temperature $T \ll \Delta/k_B$, where Δ is the difference between energies of eigenstates $|0\rangle$ and $|1\rangle$, we may achieve its relaxation into the lowest-energy state. (Otherwise, the relaxation may be to one of states with equal, or nearly-equal energies, combined with its measurement - see Fig. 7.8 and its discussion.) Then, if the qubit must be set into the opposite state, it may be driven there by the application of a pulse of a proper external classical “force”. For example, if actual spin- $1/2$ particles are used as qubits, a constant magnetic field may be applied in the $[x, y]$ plane for a half-period of the torque-induced spin precession - see Fig. 5.1c. However, for most qubit implementations, the basis state reversal using a half-period of rf-induced Rabi oscillations (Sec. 6.5) is more convenient.

their specially arranged interactions between each other and/or external drive “forces”. Besides these forces, during this evolution the system is supposed to be isolated from the dephasing and energy-dissipating environment, so that it may be described by a unitary operator defined in the 2^N -dimensional Hilbert space of N qubits:

$$|\alpha\rangle_{\text{out}} = \hat{U}|\alpha\rangle_{\text{in}}. \quad (8.131)$$

With the condition that the input and output states have the simple form (130), this equality reads

$$|(j_1)_{\text{out}}(j_2)_{\text{out}} \dots (j_N)_{\text{out}}\rangle = \hat{U} |(j_1)_{\text{in}}(j_2)_{\text{in}} \dots (j_N)_{\text{in}}\rangle. \quad (8.132)$$

The art of quantum computer design is selecting such unitary operators $\hat{U}$ that would:

- satisfy Eq. (132),
- be physically implementable,
- enable substantial performance advantages of the quantum computation over its classical counterpart of similar functionality, at least for some digital functions (algorithms).

I will have time to demonstrate the possibility of such advantages on just one, perhaps the simplest example – the so-called *Deutsch problem*.⁴⁸ Let us consider the family of single-bit classical Boolean functions $j_{\text{out}} = f(j_{\text{in}})$. Since both j are Boolean variables, i.e. may take only values 0 and 1, there are evidently only 4 such functions:

f	$f(0)$	$f(1)$	class	F	$f(1)-f(0)$
f_1	0	0	constant	0	0
f_2	0	1	balanced	1	1
f_3	1	0	balanced	1	-1
f_4	1	1	constant	0	0

(8.133)

Of them, functions f_1 and f_4 , whose values are independent of their arguments, are called *constants*, while functions f_2 (called “YES” or “IDENTITY”) and f_3 (“NOT” or “INVERSION”) are called *balanced*. The Deutsch problem is to determine the class of a single-bit function, implemented as a “black box”, as being either constant or balanced, using just one experiment.

Classically, this is clearly impossible, and the simplest way to perform the function classification involves two similar black boxes f – see Fig. 3a.

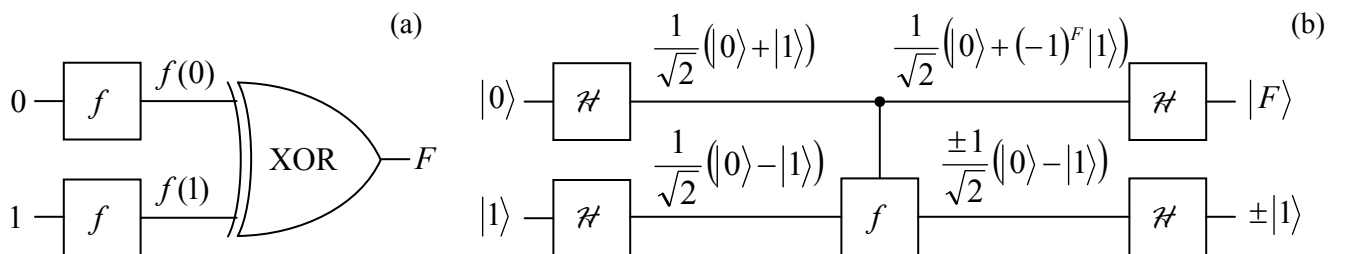


Fig. 8.3. The simplest (a) classical and (b) quantum ways to classify a single-bit Boolean function f .

⁴⁸ Named after D. Deutsch, whose 1985 paper (motivated by an inspirational but not very specific publication by R. Feynman in 1982) launched the whole field of quantum computation.

This solution uses the so-called *exclusive-OR* (for short, XOR) *gate* whose output is described by the following function F of its two Boolean arguments j_1 and j_2 :

$$F(j_1, j_2) \equiv j_1 \oplus j_2 \equiv \begin{cases} 0, & \text{if } j_1 = j_2, \\ 1, & \text{if } j_1 \neq j_2. \end{cases} \quad (8.134)$$

In the circuit shown in Fig. 3a, the gate produces output

$$F = f(0) \oplus f(1), \quad (8.135)$$

equal to 1 if $f(0) \neq f(1)$, i.e. if function f is balanced, and 0 in the opposite case - see the 4th column in Eq. (133).⁴⁹

On the other hand, let us assume that all four functions f may be implemented quantum-mechanically, for example as a unitary transform acting on two qubits (Fig. 4a), and acting as follows each of basis components $|j_1 j_2\rangle \equiv |j_1\rangle|j_2\rangle$ of the general input state (126):

$$\hat{f}|j_1\rangle|j_2\rangle = |j_1\rangle|j_2 \oplus f(j_1)\rangle, \quad (8.136)$$

where f is any of the classical Boolean functions defined by Eq. (133).

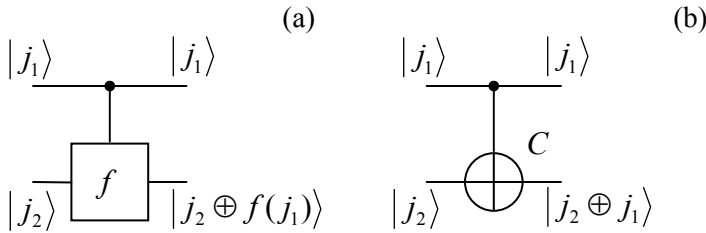


Fig. 8.4. Two-qubit quantum gates: (a) two-qubit function f and (b) its particular case C (CNOT), and their actions on the basis states.

In the particular case when f is the YES function: $f(j) = f_2(j) = j$, gate f is reduced to the so-called *CNOT gate* - a key ingredient of other quantum computation schemes, performing transform

$$\hat{C}|j_1 j_2\rangle = |j_1\rangle|j_2 \oplus j_1\rangle. \quad (8.137a) \quad \text{CNOT function}$$

Let us spell out this rule for all four possible input qubit combinations:

$$\hat{C}|00\rangle = |00\rangle, \quad \hat{C}|01\rangle = |01\rangle, \quad \hat{C}|10\rangle = |11\rangle, \quad \hat{C}|11\rangle = |10\rangle. \quad (8.137b)$$

In plain English, this means that acting on basis states $|j_1 j_2\rangle$, the CNOT gate leaves the state of first, *source* qubit (shown by the upper lines in Fig. 4) intact, but flips the state of the second, *target* qubit if the first one is in the basis state $|1\rangle$. In even simpler words, the state j_1 of the source qubit controls the NOT function acting on the target qubit - hence the gate's name CNOT (the semi-acronym of "Controlled NOT").

⁴⁹ Alternatively, we may perform two sequential experiments on the same black box f , first recording and then recalling their results.

For the quantum function (136), the Deutsch problem may be solved within the general scheme shown in Fig. 2, with the particular structure of the unitary-transform box U spelled out in Fig. 3b, which involves just one implementation of the function. Here the single-qubit quantum gate $\hat{\mathcal{H}}$ symbolizes the so-called *Hadamard* (or “Walsh-Hadamard”) *transform*⁵⁰ whose linear operator is defined by the following actions on qubit’s basis states:

Hadamard
transform

$$\hat{\mathcal{H}}|0\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle), \quad \hat{\mathcal{H}}|1\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle), \quad (8.138)$$

- see also the 4 left state labels in Fig. 3b.⁵¹ On the Bloch sphere (Fig. 5.1), and in the usual spin- $\frac{1}{2}$ notation, Eqs. (137) correspond to the transfer of the representing point from the North Pole’s state $\uparrow$, i.e. one of the eigenstates of matrix σ_z , to one of equatorial states, $\rightarrow$, i.e. one of the eigenstates of matrix σ_x , and from the South Pole state $\downarrow$ to the another equatorial state, $\leftarrow$, see Eq. (4.122). However, a $\pi/2$ -rotation in the $[x, z]$ plane would be a poor interpretation of this function. Indeed, since its operator has to be linear (to be physically realistic), it needs to perform action (138) on the basis states even when they are parts of an arbitrary linear superposition – as they are, e.g., for the two right Hadamard gates in Fig. 3b. For example, as immediately follows from Eq. (137) and operator’s linearity,

$$\hat{\mathcal{H}}(\hat{\mathcal{H}}|0\rangle) = \hat{\mathcal{H}}\left(\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)\right) = \frac{1}{\sqrt{2}}(\hat{\mathcal{H}}|0\rangle + \hat{\mathcal{H}}|1\rangle) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) + \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)\right) = |0\rangle, \quad (8.139a)$$

Absolutely similarly, we may get⁵²

$$\hat{\mathcal{H}}(\hat{\mathcal{H}}|1\rangle) = |1\rangle. \quad (8.139b)$$

Due to this reason, a better interpretation of the Hadamard transform is a π -rotation about the axis that bisects the angle between axes x and z .

Now let us carry out an analysis of the “circuit” shown in Fig. 3b, minding all the time the operator linearity, and the fact that the transformation rules (136)-(138) are only applicable to basis kets of the initial (“input”) state vector. In particular, taking into account that according to Fig. 3b, the input states of gate f in this particular circuit are described by Eqs. (138), its output state’s ket is

$$\hat{f}(\hat{\mathcal{H}}|0\rangle\hat{\mathcal{H}}|1\rangle) = \hat{f}\left(\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)\frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)\right) = \frac{1}{2}(\hat{f}|00\rangle - \hat{f}|01\rangle + \hat{f}|10\rangle - \hat{f}|11\rangle). \quad (8.140)$$

Now we may apply Eq. (136) to each of the basis kets to get:

$$\begin{aligned} \hat{f}|00\rangle - \hat{f}|01\rangle + \hat{f}|10\rangle - \hat{f}|11\rangle &\equiv \hat{f}|0\rangle|0\rangle - \hat{f}|0\rangle|1\rangle + \hat{f}|1\rangle|0\rangle - \hat{f}|1\rangle|1\rangle \\ &= |0\rangle|0 \oplus f(0)\rangle - |0\rangle|1 \oplus f(0)\rangle + |1\rangle|0 \oplus f(1)\rangle - |1\rangle|1 \oplus f(1)\rangle \quad (8.141) \\ &= |0\rangle(|0 \oplus f(0)\rangle - |1 \oplus f(0)\rangle) + |1\rangle(|0 \oplus f(1)\rangle - |1 \oplus f(1)\rangle). \end{aligned}$$

⁵⁰ In order to exclude any chance of confusion between the Hadamard transform’s operator $\hat{\mathcal{H}}$ and the Hamiltonian operator $\hat{H}$, I have typeset them using different fonts.

⁵¹ Note that according to Eq. (138), operator $\hat{\mathcal{H}}$ does *not* belong to the limited class $\hat{U}$ described by Eq. (132).

⁵² Since states 0 and 1 form a full basis of the single qubit, Eqs. (139) may be summarized as an operator equality: $\hat{\mathcal{H}}^2 = \hat{I}$.

Note that the expression in the first parentheses, characterizing the state of the target qubit, is equal to $(|0\rangle - |1\rangle) \equiv (-1)^0(|0\rangle - |1\rangle)$ if $f(0) = 0$ (and hence $0 \oplus f(0) = 0$ and $1 \oplus f(0) = 1$), and to $(|1\rangle - |0\rangle) \equiv (-1)^1(|0\rangle - |1\rangle)$ in the opposite case $f(0) = 1$, so that both cases may be described in one shot by rewriting the parentheses as $(-1)^{f(0)}(|0\rangle - |1\rangle)$. The second parentheses is absolutely similarly controlled by the value of $f(1)$, so that the state of the system at the output of gate f is unentangled again:

$$\hat{f}(\hat{\mathcal{H}}|0\rangle\hat{\mathcal{H}}|1\rangle) = \frac{1}{2}((-1)^{f(0)}|0\rangle + (-1)^{f(1)}|1\rangle)(|0\rangle - |1\rangle) = \pm \frac{1}{\sqrt{2}}(|0\rangle + (-1)^F|1\rangle)\frac{1}{\sqrt{2}}(|0\rangle - |1\rangle), \quad (8.142)$$

where the last transition has used the fact that the Boolean function F , defined by Eq. (135), equals to $\pm[f(1) - f(0)]$ – compare the last two columns in Eq. (133). Since the common sign (i.e. the common phase shift by π) is inconsequential, it may be prescribed to any of the component ket-vectors – for example to that of the target qubit, as shown by the third pair of state labels in Fig. 3b.

This intermediate result is already rather remarkable. Indeed, it shows that, despite the impression one could get from Fig. 4, gates f and even C , being “controlled” by the source qubit, may change that qubit’s state as well! This fact (partly reflected by the vertical direction of the control lines in Figs. 3, 4, symbolizing the same stage of system’s evolution in time) shows how careful one should be interpreting quantum-computational “circuits”.

At the second stage of the circuit shown in Fig. 3b, the qubit components of state (142) are fed into one more pair of Hadamard gates, whose outputs therefore are

$$\hat{\mathcal{H}}\frac{1}{\sqrt{2}}(|0\rangle + (-1)^F|1\rangle) = \frac{1}{\sqrt{2}}(\hat{\mathcal{H}}|0\rangle + (-1)^F\hat{\mathcal{H}}|1\rangle), \quad \text{and} \quad \hat{\mathcal{H}}\left(\pm\frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)\right) = \pm\frac{1}{\sqrt{2}}(\hat{\mathcal{H}}|1\rangle - \hat{\mathcal{H}}|0\rangle). \quad (8.143)$$

Now using Eqs. (138) again, we see that the output state ket-vectors of the source and target qubits are, respectively,

$$\frac{1 + (-1)^F}{2}|0\rangle + \frac{1 - (-1)^F}{2}|1\rangle, \quad \text{and} \quad \pm|1\rangle. \quad (8.144)$$

Since, according to Eq. (135), the Boolean function F may take only values 0 or 1, the final state of the source qubit is always one of its basis states j , namely the one with $j = F$. Its measurement (see Fig. 2) immediately tells us whether function f , participating in Eq. (136), is constant or balanced.⁵³

Thus, the quantum circuit shown in Fig. 3b indeed solves the Deutsch problem in one shot. Reviewing our analysis, we may see that this is possible because the unitary transform performed by gate f is applied to quantum superpositions (138) rather than to the basis states. Due to this trick, the quantum state components depending on $f(0)$ and $f(1)$ are processed simultaneously, in parallel. This *quantum parallelism* may be extended to circuits with many ($N \gg 1$) qubits and, for some tasks, provide a dramatic performance increase – for example, reducing the necessary circuit component number from $O(\exp\{N\})$ to $O(N^p)$, where p is a finite (and not very big) number.

⁵³ This means that the last Hadamard transform of the target qubit (i.e. the Hadamard gate shown in the lower right corner of Fig. 3b) is not necessary for the Deutsch problem solution – though it should be included if we want the whole circuit to satisfy the general condition (132).

However, this efficiency comes at a high price. Indeed, let us discuss the physical implementation of quantum gates, starting from the Hadamard gate, which performs a single-qubit transform - see Eq. (138). With the linearity requirement, its action on the arbitrary state (125) should be

$$\hat{H}|\alpha\rangle = a_0\hat{H}|0\rangle + a_1\hat{H}|1\rangle = a_0\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) + a_1\frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) = \frac{1}{\sqrt{2}}(a_0 + a_1)|0\rangle + \frac{1}{\sqrt{2}}(a_0 - a_1)|1\rangle, \quad (8.145)$$

meaning that the state expansion coefficients in the end ($t = T$) and beginning ($t = 0$) of the qubit evolution in time have to be related as

$$a_0(T) = \frac{a_0(0) + a_1(0)}{\sqrt{2}}, \quad a_1(T) = \frac{a_0(0) - a_1(0)}{\sqrt{2}}. \quad (8.146)$$

This task may be again performed using the Rabi oscillations, which were discussed in Sec. 6.5, i.e. by applying to the qubit (a two-level system), for a limited time period T , a weak sinusoidal external signal of frequency ω equal to the intrinsic quantum oscillation frequency $\omega_{nn'}$, defined by Eq. (6.85). A perturbative analysis of the Rabi oscillations was carried out in Sec. 6.5, even for nonvanishing (though small) detuning $\Delta = \omega - \omega_{nn'}$, but only for the particular initial conditions when at $t = 0$ the system was in one on the basis states (there labeled as n'), i.e. another state (there labeled n) was empty. For our current purposes we need to find coefficients $a_{0,1}(t)$ of expansion (125) for arbitrary initial conditions $a_{0,1}(0)$, subject only to the time-independent normalization condition $|a_0|^2 + |a_1|^2 = 1$. For the case of exact tuning, $\Delta = 0$, the solution of Eqs. (6.94) is elementary, and gives, instead of Eq. (6.102),⁵⁴ the following solutions:

$$\begin{aligned} a_0(t) &= a_0(0)\cos\Omega t - ia_1(0)e^{i\varphi}\sin\Omega t, \\ a_1(t) &= a_1(0)\cos\Omega t - ia_0(0)e^{-i\varphi}\sin\Omega t, \end{aligned} \quad (8.147)$$

where Ω is the Rabi oscillation frequency (6.101), in the exact-tuning case proportional to amplitude $|A|$ of the external rf drive $A = |A|\exp\{i\varphi\}$, while φ is the phase of the driving signal – see Eqs. (6.86)-(6.87). Comparing these expressions with Eqs. (146), we see that for $t = T = \pi/4\Omega$ and $\varphi = \pi/2$ they “almost” coincide, besides the opposite sign of $a_1(T)$.

Conceptually the simplest way to correct this deficiency is to follow the rf “ $\pi/4$ -pulse”, just discussed, by a short dc “ π -pulse” of duration $T' = \pi/\delta$, which temporary creates an small additional energy difference δ between basis states 0 and 1. According to the basic Eq. (1.61), such difference creates an additional phase difference $T'\delta/\hbar$ between the states, equal to π for the “ π -pulse”.

Another way (that may be also useful for two-qubit operations) is to use another, auxiliary energy level E_2 whose distances from the basic levels E_1 and E_0 are significantly different from the difference $(E_1 - E_0)$ – see Fig. 5a. In this case, the weak external rf field tuned to any of 3 potential quantum transition frequencies $\omega_{nn'} \equiv (E_n - E_{n'})/\hbar$ initiates such transitions between the corresponding states only, with a negligible perturbation of the state not involved in this transition. Such transitions may be again described by Eqs. (147), with the appropriate index changes. For the Hadamard transform implementation, it is sufficient to apply (after the already discussed $\pi/4$ -pulse of frequency ω_{10} , and with

⁵⁴ To comply with our current notation, coefficients $a_{n'}$ and a_n of Sec. 6.5 should be replaced with a_0 and a_1 . Also note that their definition (6.82) implies that the trivial time evolution (6.81) of unperturbed qubits has been already excluded from these expansion coefficients.

the initially empty level E_2), an additional π -pulse of frequency ω_{20} , with any phase φ . Indeed, according to the first of Eqs. (147), with the due replacement $a_1(0) \rightarrow a_2(0) = 0$, such pulse flips the sign of coefficient $a_0(t)$, while coefficient $a_1(t)$, not involved in this additional transition, remains unchanged.

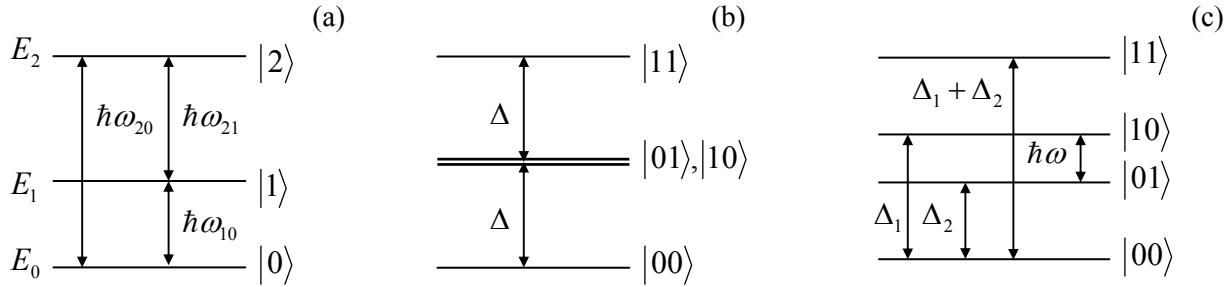


Fig. 8.5. Energy-level schemes used for unitary transformations of (a) single qubits and (b, c) two-qubit systems.

Now let me describe the conceptually simplest (though, for some qubit types, not practically most convenient) scheme for the implementation of the CNOT gate, whose action is described by a linear unitary operator satisfying Eq. (137). For that, evidently, qubits have to let interact for some time T . As was repeatedly discussed in two past chapters, in most cases such interaction of two subsystems is bilinear – see, e.g., Eq. (6.148). For qubits, i.e. two-level systems, each of the component operators may be represented by a 2×2 matrix in the basis of states 0 and 1. According to Eq. (4.105), such matrix may be expressed as a linear combination $(c_0 I + \mathbf{c} \cdot \boldsymbol{\sigma})$, where c_0 and three Cartesian components of vector $\mathbf{c}$ are c -numbers. Let us take such bilinear interaction Hamiltonian in the simplest form

$$\hat{H}_{\text{int}}(t) = \begin{cases} \kappa \hat{\sigma}_z^{(1)} \hat{\sigma}_z^{(2)}, & \text{for } 0 < t < T, \\ 0, & \text{otherwise,} \end{cases} \quad (8.148)$$

where the upper index is the qubit number, and κ is a c -number constant.⁵⁵ According to Eq. (4.175), by the end of the interaction period, this Hamiltonian produces the following unitary transform:

$$\hat{U}_{\text{int}} = \hat{I} \exp \left\{ -\frac{i}{\hbar} \hat{H}_{\text{int}} T \right\} = \hat{I} \exp \left\{ -\frac{i}{\hbar} \kappa \hat{\sigma}_z^{(1)} \hat{\sigma}_z^{(2)} T \right\}. \quad (8.149)$$

Since in the basis of unperturbed two-bit states $|j_1 j_2\rangle$ the product operator $\hat{\sigma}_z^{(1)} \hat{\sigma}_z^{(2)}$ is diagonal, so is the unitary operator (149), with the following action on the basis states:

$$\hat{U}_{\text{int}} |j_1 j_2\rangle = \exp \{ i \theta \sigma_z^{(1)} \sigma_z^{(2)} \} |j_1 j_2\rangle, \quad (8.150)$$

⁵⁵ The assumption of simultaneous time independence of the basis state vectors and the interaction operator (within the time interval $0 < t < T$) is possible only if the basis state energy difference Δ of both qubits is exactly the same. For this case, the simple physical explanation of the time evolution (149) follows from Fig. 8.5, which shows the spectrum of the total energy $E = E_1 + E_2$ of the two-bit system. In the absence of interaction, the energies of two basis states, $|01\rangle$ and $|10\rangle$, are equal, enabling even a weak qubit interaction to cause their substantial evolution in time – see Sec. 6.7. If the qubit energies are different (Fig. 5c), the interaction may still be reduced, in the rotating-wave approximation, to Eq. (149), by compensating the energy difference $(\Delta_1 - \Delta_2)$ with an external rf signal of frequency $\omega = (\Delta_1 - \Delta_2)/\hbar$ – see Sec. 6.5.

where $\theta \equiv -\kappa T/\hbar$, and σ_z are the eigenvalues of the Pauli matrix σ_z for the basis states of the corresponding qubit: $\sigma_z = +1$ for $|j\rangle = |0\rangle$, and $\sigma_z = -1$ for $|j\rangle = |1\rangle$. Let me, for clarity, spell out Eq. (150) for the particular case $\theta = -\pi/4$ (corresponding to the qubit coupling time $T = \pi\hbar/4\kappa$):

$$\hat{U}_{\text{int}}|00\rangle = e^{-i\pi/4}|00\rangle, \quad \hat{U}_{\text{int}}|01\rangle = e^{i\pi/4}|01\rangle, \quad \hat{U}_{\text{int}}|10\rangle = e^{i\pi/4}|10\rangle, \quad \hat{U}_{\text{int}}|11\rangle = e^{-i\pi/4}|11\rangle. \quad (8.151)$$

In order to compensate the undesirable parts of this joint phase shift of the basis states, let us apply (either before or after it) similar individual “rotations” of each qubit by angle $\theta' = +\pi/4$, using the following product of two independent operators, plus (just for the result clarity) a common, and hence inconsequential, phase shift $\theta'' = -\pi/4$:⁵⁶

$$\hat{U}_{\text{com}} = \hat{I} \exp\{i\theta'(\hat{\sigma}_z^{(1)} + \hat{\sigma}_z^{(2)}) + i\theta''\} = \hat{I} \exp\left\{i\frac{\pi}{4}\hat{\sigma}_z^{(1)}\right\} \exp\left\{i\frac{\pi}{4}\hat{\sigma}_z^{(2)}\right\} \exp\left\{-i\frac{\pi}{4}\right\}. \quad (8.152)$$

Since this operator is also diagonal in the $|j_1 j_2\rangle$ basis, it is equally easy to calculate the change of the basis states by the total unitary operator $\hat{U}_t \equiv \hat{U}_{\text{com}} \hat{U}_{\text{int}}$:

$$\hat{U}_t|00\rangle = |00\rangle, \quad \hat{U}_t|01\rangle = |01\rangle, \quad \hat{U}_t|10\rangle = |10\rangle, \quad \hat{U}_t|11\rangle = -|11\rangle. \quad (8.153)$$

This result already shows the main “miracle action” of two-qubit gates, such as shown in Fig. 4: the source qubit is left intact (only if it is in a basis state!), while the state of the target qubit is altered. True, this is still different from the CNOT operator’s action (137), but may be readily reduced to it by its sandwiching of transform U_t between two Hadamard transforms applied to the target qubit:

$$\hat{C} = \frac{1}{2} \hat{\mathcal{H}}^{(2)} \hat{U}_t \hat{\mathcal{H}}^{(2)}. \quad (8.154)$$

We have spend quite a bit of time on the discussion of the CNOT gate,⁵⁷ and now I can reward the reader for his/her effort with a bit of good news: it has been proved that an *arbitrary* unitary transform that satisfies Eq. (132), i.e. may be used within the general scheme outlined in Fig. 2, may be decomposed into a set of CNOT gates mixed with simpler single-qubit gates - for example, the Hadamard gate plus the $\pi/2$ rotation discussed above.⁵⁸ Unfortunately, I have no time for a detailed discussion of more complex circuits.⁵⁹ Perhaps the most famous of them is the scheme for integer

⁵⁶ It Eq. (4.175) shows, each of component unitary transforms $\hat{I} \exp\{i\theta' \hat{\sigma}_z\}$ may be created by applying to each qubit, for a time period $T' = \hbar\theta'/\kappa'$, a constant external field described by Hamiltonian $\hat{H} = -\kappa' \hat{\sigma}_z$. We already know that for a charged, spin- $1/2$ particle, such Hamiltonian may be created by applying z -oriented external constant magnetic field – see Eq. (4.163). For most other physical implementations of qubits, the organization of such Hamiltonian is also straightforward – see, e.g., Fig. 7.4 and its discussion.

⁵⁷ As was discussed above, this gate is identical to quantum gate f for $f=f_3$, i.e. $f(j)=j$. The implementation of f for 3 other functions f requires straightforward modifications whose analysis is left for reader’s exercise.

⁵⁸ This fundamental importance of the CNOT gate was perhaps a major reason why D. Wineland, the leader of the NIST group that had demonstrated the first experimental implementation in 1995 (following the theoretical suggestion by J. Cirac and P. Zoller), was awarded the 2012 Nobel Prize (shared with S. Haroche, the leader of another leading group working towards quantum computation).

⁵⁹ For that, the reader may be referred to either the monograph by Nielsen and Chuang, cited above, or to a shorter (but more formal) textbook by N. Mermin, *Quantum Computer Science*, Cambridge U. Press, 2007.

number factoring, suggested in 1994 by P. Shor.⁶⁰ Due to its potential practical importance for breaking broadly used communication encryption schemes such as the RSA code,⁶¹ this opportunity has incited a huge wave of enthusiasm, and triggered experimental efforts to implement quantum gates and circuits using a broad variety of two-level quantum systems. Presently, the following options are most eagerly pursued:⁶²

(i) Trapped ions. The first experimental demonstrations of quantum state manipulation (including the already mentioned first CNOT gate) have been carried out using deeply cooled atoms in optical traps, similar to those used in frequency and time standards. Their electron spins are natural qubits, whose states may be manipulated using the Rabi transfers excited by suitably tuned lasers. The spin interactions with environment may be very weak, resulting in large dephasing times (T_2 , see Sec. 7.3), up to a few seconds. Since the distances between atoms in the traps are relatively large (of the order of a micron), their direct spin-spin interaction is even weaker, but atoms may be made effectively interacting either via their mechanical oscillations about the potential minima of the trapping field, or via photons in electromagnetic resonators (“cavities”).⁶³ Perhaps the main challenge of using this approach for quantum computation is poor “scalability”, i.e. the enormous challenge of creating large, ordered systems of individually addressable qubits.

(ii) Nuclear spins are also typically very weakly connected to environment, with T_2 exceeding 10 seconds in some cases. Their eigenenergies E_0 and E_1 may be split by external dc magnetic fields (typically, of the order of 10 T), while the interstate Rabi transfers may be readily achieved by application of external rf fields with frequencies $\omega = (E_1 - E_0)/\hbar$ of a few hundred MHz.⁶⁴ The challenges of this option include the weakness of spin-spin interactions (typically mediated through molecular electrons), resulting in a very slow spin evolution, whose time scale $\hbar/\kappa$ may become comparable with T_2 , and small level separations $E_1 - E_0$, corresponding to a few K,⁶⁵ i.e. much smaller than the room temperature, creating a problem with qubit state preparation.⁶⁶

Despite these challenges, the nuclear spin option was used for the first implementation of the Shor algorithm for factoring of a small number ($15 = 5 \times 3$) as early as in 2001.⁶⁷ However, the extension of this success to larger systems, beyond the set of spins inside one molecule, is problematic.

(iii) Josephson-junction devices. Much better scalability may be achieved with solid state devices, especially in superconductor integrated circuits including weak contacts - Josephson junctions. As was already discussed in Sec. 2.8, if the coupling of a Josephson junction to its dissipative environment is sufficiently weak (in particular if its effective parallel resistance is much higher than the

⁶⁰ His original paper was published only in proceedings of a meeting, but a clear description of the algorithm may be found in several accessible sources including *Wikipedia* (http://en.wikipedia.org/wiki/Shor's_algorithm).

⁶¹ Named after R. Rivest, A. Shamir, and L. Adleman, the authors of the first open publication of the code in 1977, but actually invented earlier (in 1973) by C. Cocks.

⁶² For more details, and a discussion of other possible implementations (such as quantum dots and dopants in crystals) see, e.g., T. Ladd *et al.*, *Nature* **464**, 45 (2010), and references therein.

⁶³ A brief discussion of such interactions (so-called Cavity QED) will be given in Sec. 9.4 below.

⁶⁴ In this field, the condition $\omega = \omega_{10}$, discussed above, is called the *nuclear magnetic resonance*, or NMR – the term well known due to the broad application of this effect in chemistry and medicine.

⁶⁵ See Eq. (4.5) and its discussion.

⁶⁶ This challenge may be partly mitigated using ingenious spin manipulation techniques such as *refocusing* – see, e.g., either Sec. 7.7 in Nielsen and Chuang, or J. Keeler’s monograph cited in the end of Sec. 6.5.

⁶⁷ B. Lanyon *et al.*, *Phys. Rev. Lett.* **99**, 250505 (2001).

quantum resistance unit $R_Q \sim 10^4 \Omega$), the Josephson phase variable φ behaves as a coordinate of a 1D quantum particle with effective mass (2.252), moving in a 2π -periodic potential - see Eq. (2.250). This fact creates several opportunities for qubit implementation using quantum behavior of this *macroscopic* degree of freedom.

In an insulated junction,⁶⁸ the phase motion in the periodic potential $U(\varphi) = -E_J \cos \varphi$ creates the energy band structure $E(q)$ that was discussed in detail in Sec. 2.7. In particular, in the weak potential limit (which, for the Josephson junction case, is valid at $E_J \ll e^2/2C$ – see the discussion in Sec. 2.8), the lowest bandgaps are very narrow, and function $E(q)$ in their vicinity is well described by the usual level anticrossing – see Figs. 2.28 and 2.29 and their discussion. The translation of this fact to the Josephson junction language (see, in particular, Eq. (2.256) and its discussion) shows that the values of the effective electric charge Q of the junction, on two anticrossing energy branches, differ by charge $2e$ of one Cooper pair. Since, according to Eq. (2.222) and its discussion, the system dynamics in this case is reduced to the interaction of these two states with different Q , in application to quantum computation this system is called the *charge qubit*. Unfortunately, the states of such qubit are rather sensitive to random charged impurities in junction's vicinity, causing strong fluctuations, and hindering its control, so this option is not actively pursued nowadays.

Other options are based on the modification of potential $U(\varphi)$ at Josephson junction incorporation into superconducting loops, i.e. in SQUIDs.⁶⁹ In the simplest case of a single loop of inductance L closed by one junction with critical current I_C , the total potential energy of the system in an external magnetic field is⁷⁰

$$U(\varphi) = E_J \left[\frac{(\varphi - \varphi_{\text{ext}})^2}{2\beta_L} - \cos \varphi \right], \quad \text{with } E_J = \frac{\hbar I_C}{2e}, \quad \beta_L \equiv \frac{4eI_C L}{\hbar}, \quad (8.155)$$

where φ_{ext} is proportional to the external magnetic flux Φ_{ext} through the loop. According to this relation, at $E_J \gg e^2/2C$ (corresponding to the tight-binding limit of the energy band theory), one convenient way to implement a two-level system is to take the dimensionless inductance parameter β_L above but very close to 1 ($0 < \beta_L - 1 \ll 1$), the “symmetrizing” magnetic field ($\varphi_{\text{ext}} \approx \pi$), and $E_J \approx (e^2/C)/(\beta_L - 1)^3$. In this case, the potential profile has the shape of a nearly symmetrical double well, with ground states in each well coupled by tunneling through a relatively low tunnel barrier, creating a pair of eigenstates with relatively low eigenenergy splitting $\Delta = E_1 - E_0 \ll E_J$ (Fig. 6a).

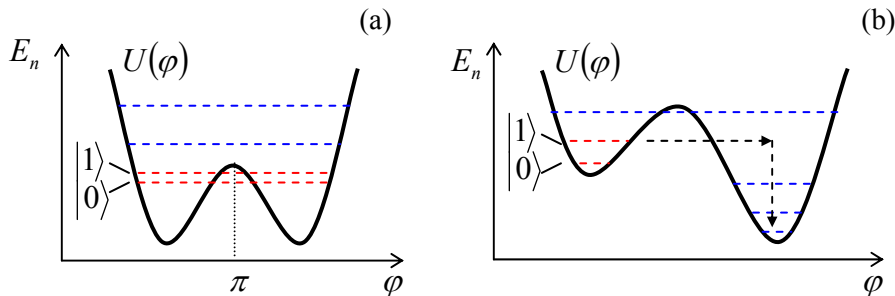


Fig. 8.6. Typical potential profiles and energy levels of SQUID-based qubits: (a) “flux qubit” and (b) “phase qubit”. Red dashed lines show eigenenergies of the used states 0 and 1.

⁶⁸ For the purposes of E_J control reasons, it is more convenient to use two-junction configurations called *Bloch transistors*. Unfortunately, I do not have time to go into these details.

⁶⁹ See, e.g., EM Sec. 6.4 and references therein.

⁷⁰ This expression directly follows from combining EM Eqs. (6.57), (6.59), and (6.70).

Such *flux qubits* have a relatively large magnitude $|\Phi_{10}| = |\Phi_{01}|$ of the matrix elements of the operator of magnetic flux $\Phi = (\hbar/2e)\varphi$ piercing the SQUID loop. This certainly makes the arrangement of necessary coupling between flux qubits (see, e.g., Eq. (149) and its discussion) very easy, despite the macroscopic ($\sim 10\ \mu\text{m}$) sizes of SQUIDs and hence of the distances between them, decreasing the time $T \sim \hbar/\kappa$ necessary for the most critical two-bit (e.g., CNOT) operations, to a just few nanoseconds. However, the large flux matrix elements also increase the undesirable coupling of such qubits to dephasing environment, and hence decrease dephasing time T_2 – typically, to just a few tens or hundreds nanoseconds, uncomfortably close to T .

This coupling may be decreased, leading to a substantial increase of T_2 (up to a few microseconds) by moving the bias phase φ_{ext} away from the symmetrizing value π , i.e. using the asymmetric potential profile sketched in Fig. 6b. The working states 0 and 1 of such *phase qubit*, localized in a higher potential well (shown left in Fig. 6b), are actually metastable, but with a very long lifetime because of the relatively high barrier separating the wells. An additional benefit of this arrangement is that a fast lowering of the tunnel barrier causes the system in state 1 to tunnel into the lower well, with the sequential energy relaxation (see the arrows in Fig. 6b); this process be used for qubit state readout. A major problem of phase qubits is that the part of potential $U(\varphi)$, in which qubit states are localized, is almost quadratic, so that the energy levels are nearly equidistant – cf. Eqs. (2.114), (6.15), and (6.22).⁷¹ As a result, the external rf drive of frequency $\omega = (E_1 - E_0)/\hbar$, used to arrange the state transforms described by Eq. (146), may induce simultaneous undesirable transitions to (and between) higher energy levels. This effect may be mitigated by the rf drive amplitude reduction (see Problem 6.6), but at a price of the proportional increase of transfer time T , that may again become comparable to T_2 . Despite this problem, phase qubits have been used for a successful experimental demonstration of the core single-operand and two-operand gates, and recently, for the reproduction of number 15 factoring “48% of the time”.⁷²

(iv) Optical systems pose a special challenge for quantum computation: due to the virtual linearity of most electromagnetic media at reasonable light power, the implementation of interaction Hamiltonians, such as (149), is problematic. However, in 2001 a very smart way around this hurdle was invented.⁷³ In this *KLM scheme*, nonlinear elements are not needed, and quantum gates may be composed just of linear devices (such as optical waveguides, mirrors and beam splitters), plus single-photon sources and detectors. Unfortunately, a quantitative discussion of this scheme would require using the basics of quantum electrodynamics that will be discussed only in the next chapter. The work in this direction has already led to an experimental demonstration of factoring number $21 = 3 \times 7$ (which in some aspects is easier than that of 15).⁷⁴

Let me, however, note that due to the statistical nature of Shore’s algorithm, and the so-far imperfect fidelity of qubit manipulations, all number factoring experiments carried out so far may be more fairly described merely as demonstrations of their result *consistency* with the (evident) mathematical facts. So, despite a very substantial research effort, the progress is rather slow, with the

⁷¹ This is even more true for the so-called “transmons” (or “Xmons”) – the phase qubits versions in which a Josephson junction is just a part of an external resonator, providing it with small nonlinearity (anharmonism) – see, e.g., R. Barrens *et al.*, *Nature* **508**, 500 (2014) and references therein.

⁷² E. Lucero *et al.*, *Nature Physics* **8**, 719 (2012).

⁷³ E. Knill *et al.*, *Nature* **409**, 46 (2001).

⁷⁴ E. Martín-López *et al.*, *Nature Photonics* **6**, 773 (2012).

main culprit being the unintentional coupling of qubits to environment, leading most importantly to their state dephasing, and eventually to errors. (Another major problem of this research field is the lack of algorithms (besides Shor's number factoring) that would give quantum computation a substantial advantage over classical counterparts, and hence a potential customer base broader than the communication encryption community, that could provide the necessary significant support.)

Of course, some error probability exists in classical digital logic gates and memory cells as well. However, in this case, there is no conceptual problem with the device state measurement, so that the error may be detected and corrected in many ways; perhaps the simplest one is the so-called *majority voting*. For that, the input bit is reproduced in several (say, three) copies and sent to three similar devices whose outputs are measured and compared. If the output bits differ, at least one of the devices has made an error. The error may be not only *detected*, but also *corrected* by taking the two coinciding output bits for the correct one. If the probability of a single device error is $W \ll 1$, the probability of error of any device pair is close to W^2 , and that of *some* pair (and hence of the whole majority voting scheme) is close to $3W^2$. Since for the currently dominating CMOS integrated circuits, W is very small, such error correction circuit creates a dramatic fidelity improvement – at the cost of higher circuit complexity (which may be traded for larger time delay) and consumed power.

For quantum computation, the general idea of using several devices (say, qubits) for coding the same information remains the same; however, there are two major complications, both due to the analog nature of qubit states. First, as we know from Chapter 7, the dephasing effect of environment may be described as a slow random drift of coefficients a_j in expansion (128), leading to the deviation of the output state α_{fin} from the basis form (132), and hence to a nonvanishing probability of wrong qubit state readout (Fig. 2). Hence the quantum error correction has to protect the result not only against possible random state flips $0 \leftrightarrow 1$ as in the classical digital computer, but also against these “creeping” analog errors.

Second, the qubit state is impossible to copy exactly (*clone*) without disturbing it, as follows from the following simple calculation.⁷⁵ Cloning state α of one qubit to another qubit, initially in an independent state (say the basis state 0), means the following transformation of the two-qubit ket: $|\alpha 0\rangle \rightarrow |\alpha \alpha\rangle$. If we want such transform to be performed by a real quantum system whose evolution is described by a unitary operator $\hat{u}$, and to be correct for an arbitrary state α , it has to work not only for both basis states of the qubit:

$$\hat{u}|00\rangle = |00\rangle, \quad \hat{u}|10\rangle = |11\rangle, \quad (8.156)$$

and also for their arbitrary linear combination (125). Since operator $\hat{u}$ has to be linear, we may use Eq. (156) to calculate

$$\hat{u}|\alpha 0\rangle = \hat{u}(a_0|0\rangle + a_1|1\rangle)|0\rangle = a_0\hat{u}|00\rangle + a_1\hat{u}|10\rangle = a_0|00\rangle + a_1|11\rangle. \quad (8.157)$$

On the other hand, the desired result of cloning is

$$|\alpha \alpha\rangle = (a_0|0\rangle + a_1|1\rangle)(a_0|0\rangle + a_1|1\rangle) = a_0^2|00\rangle + a_0a_1(|10\rangle + |01\rangle) + a_1^2|11\rangle, \quad (8.158)$$

i.e. evidently different, so that, for an arbitrary α ,

⁷⁵ Amazingly, this *no-cloning theorem* was discovered as late as in 1982 (independently by W. Wootters and W. Zurek, and by D. Dieks) - in the context of work toward quantum cryptography.

$$\hat{u}|\alpha 0\rangle \neq |\alpha \alpha\rangle,$$

(8.159) No-cloning theorem

showing that the qubit state cloning is indeed impossible.⁷⁶

This problem may be circumvented in the way shown in Fig. 7a. Here the CNOT gate, whose action is described by Eq. (137), entangles an arbitrary input state (125) of the source qubit with a basis initial state of an ancillary qubit - frequently called *ancilla*. Using Eq. (137), we may readily calculate the output two-qubit state's vector:

$$|\alpha\rangle_{N=2} = \hat{C}(a_0|0\rangle + a_1|1\rangle)|0\rangle = a_0\hat{C}|01\rangle + a_1\hat{C}|10\rangle = a_0|00\rangle + a_1|11\rangle.$$

(8.160) Quasi-cloning

We see that this circuit does perform operation (157), i.e. re-prescribes the initial source qubit's expansion coefficients a_0 and a_1 equally to two qubits, i.e. duplicates the input information, though in contrast with the “genuine” cloning, it changes the state of the source qubit. Such “quasi-cloning” is the key to virtually all quantum error correction techniques.

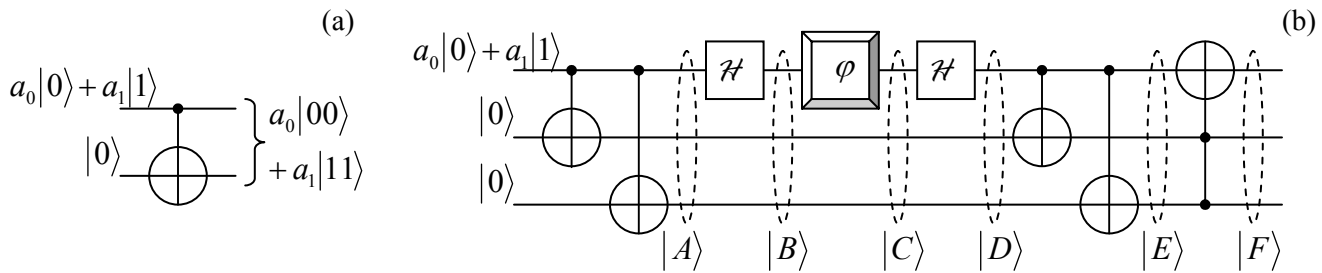


Fig. 8.7. (a) Quasi-cloning, and (b) detection and correction of dephasing errors in a single qubit.

Consider, for example, the three-qubit circuit shown in Fig. 7b. At its input, the double application of the quasi-cloning produces an intermediate state A with the ket-vector

$$|A\rangle = a_0|000\rangle + a_1|111\rangle, \quad (8.161)$$

which is an evident generalization of Eq. (160).⁷⁷ Subjecting the source qubit to the Hadamard transform (138), we get three-qubit state B represented by vector

$$|B\rangle = a_0 \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)|00\rangle + a_1 \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)|11\rangle. \quad (8.162)$$

Now let us assume that at this stage, the source qubit comes into a contact with a dephasing environment (in Fig. 7, symbolized by single-qubit “gate” ϕ). As we know from Sec. 7.3, its effect

⁷⁶ This does not mean that several qubits cannot be put into the same, arbitrary quantum state - theoretically, with arbitrary precision. Indeed, they may be first set into their lowest-energy stationary states as was discussed above, and then driven into an arbitrary state (125) by exerting on them similar classical external “forces”. So, the no-cloning theorem pertains to only an *unknown* state α of a qubit.

⁷⁷ Such state is also the 3-qubit example of the so-called *Greenberger-Horne-Zeilinger* (GHZ) states, which are frequently called the “most entangled” states of a system of $N > 2$ qubits.

(besides some inconsequential shift of *common* phase) may be described by a random *mutual* phase shift of the basis states:⁷⁸

$$|0\rangle \rightarrow e^{i\varphi}|0\rangle, \quad |1\rangle \rightarrow e^{-i\varphi}|1\rangle. \quad (8.163)$$

As a result, for the intermediate state C (see Fig. 7b) we may write

$$|C\rangle = a_0 \frac{1}{\sqrt{2}} (e^{i\varphi}|0\rangle + e^{-i\varphi}|1\rangle) |00\rangle + a_1 \frac{1}{\sqrt{2}} (e^{i\varphi}|0\rangle - e^{-i\varphi}|1\rangle) |11\rangle. \quad (8.164)$$

At this stage, in this simple theoretical model, the coupling with environment is completely quenched (ahh, if this could be possible in reality! we would have quantum computers by now :-), and the source qubit is fed into one more Hadamard gate. Using Eqs. (138) again, for state D after this gate we get

$$|D\rangle = a_0 (\cos\varphi|0\rangle + i\sin\varphi|1\rangle) |00\rangle + a_1 (i\sin\varphi|0\rangle + \cos\varphi|1\rangle) |11\rangle. \quad (8.165)$$

Now the qubits are passed through the second, similar pair of CNOT gates – see Fig. 7b. Using Eq. (137), for the ket-vector of the resulting state E we readily get expression

$$|E\rangle = a_0 \cos\varphi |000\rangle + a_0 i\sin\varphi |111\rangle + a_1 i\sin\varphi |011\rangle + a_1 \cos\varphi |100\rangle, \quad (8.166a)$$

which evidently may be grouped as

$$|E\rangle = (a_0|0\rangle + a_1|1\rangle)\cos\varphi|00\rangle + (a_1|0\rangle + a_0|1\rangle)i\sin\varphi|11\rangle. \quad (8.166b)$$

This is already a rather remarkable result. It shows that if we measure the ancilla qubits at stage E , and both results corresponded to states 0, we may be 100% sure that the source qubit (which is not affected by the measurement!) is in its initial state even after the interaction with environment. The only result of an increase of this interaction (as quantified by the magnitude of phase φ) is the growth of the probability,

$$W = \sin^2 \varphi, \quad (8.167)$$

of getting the opposite result, which signals a dephasing-induced error in the source qubit. This implicit measurement, without disturbing the source qubit, is called *quantum error detection*.

Even more impressive result may be achieved by adding to the circuit one more component, the so-called *Toffoli* (or “CCNOT”) *gate*, denoted by the rightmost symbol in Fig. 7b. This 3-qubit gate is conceptually similar to the CNOT gate discussed above, besides that it flips the basis state of its target qubit only if *both* basis states of its two source qubits are 1. (In the circuit shown in Fig. 7b, the former role is played by our source qubit, while the latter role, by two ancilla qubits.) According to its

⁷⁸ For example, in the Hilbert space of the qubit, the model Hamiltonian (7.70), which was explored in Sec. 7.3, is diagonal in the z -basis of states 0 and 1, so that the unitary transform it provides during interval T is also diagonal,

giving the phase shifts described by Eq. (163), with $\varphi = \frac{1}{\hbar} \int_0^T f\{\lambda\} dt$. Let me emphasize again that Eq. (162) is

valid only if the interaction with environment is a pure dephasing, i.e. does not include the energy relaxation of the qubit or its thermal activation to the higher eigenstate – see Chapter 7.

definition, the Toffoli gate has no effect on the first parentheses in Eq. (166b), but flips the source qubit's state in the second parentheses. The result may be factorized as follows,

$$|F\rangle = (a_0|0\rangle + a_1|1\rangle)(\cos\varphi|00\rangle + i\sin\varphi|11\rangle), \quad (8.168)$$

showing that now the source qubit is again fully unentangled from the ancilla qubits. Moreover, calculating the norm squared of the second operand, we get

$$(\cos\varphi\langle 00| - i\sin\varphi\langle 11|)(\cos\varphi|00\rangle + i\sin\varphi|11\rangle) = \cos^2\varphi + \sin^2\varphi = 1, \quad (8.169)$$

Quantum
error
correction

so that the final state of the source qubit *always, exactly* coincides with its initial state. This is the famous miracle of *quantum state correction*, taking place “automatically” - without any qubit measurements, and for any random phase shift φ .

The circuit shown in Fig. 7b may be improved by adding the Hadamard gate pairs, similar to that used for the source qubit, to the ancilla qubits as well. If dephasing is small in the sense that the W given by Eq. (167) is much less than 1, this modified circuit may provide substantial error probability reduction (to $\sim W^2$) even if the ancilla qubits are also subjected to a similar dephasing and the source qubits, at the same stage - i.e. between two Hadamard gates. The perfect automatic correction of *any* error (not only inner dephasing of a qubit and its relaxation/excitation, but also the mutual dephasing between qubits) of *any* used qubit needs even more parallelism. The first circuit of that kind, based on 9 parallel qubits, which is a natural generalization of the circuit discussed above, had been invented in 1995 by the same P. Shor. Later, 5-qubit circuits enabling similar error correction were suggested. (The further parallelism reduction has been proved impossible.)

However, all these results assume that the error correction circuits as such are perfect, i.e. completely isolated from the environment. In the real world this cannot be done. Now the key question is what maximum level $W_{\max}$ of error probability in each gate (including those in the used error correction scheme) can be automatically corrected, thus opening a way toward large quantum computers producing some useful results – first of all, the factoring of large numbers - with at least 10^3 bits to be of interest for practice. To the best of my knowledge, this critical level has not yet been strictly calculated, partly because the error correction greatly inflates the number of the total gates in the system – by a factor crudely proportional to the number N of used qubits. Various authors give broadly different estimates: from $W_{\max} \sim 10^{-6}$ to $W_{\max} \sim 10^{-2}$. Whatever the critical level is, it has not been reached yet.

This situation has motivated the search for the quantum computation schemes different from that shown in Fig. 2; the most prominent alternative is called *adiabatic quantum computation*.⁷⁹ In its most actively pursued option (for which “quantum system modeling” would be a more appropriate name), the interaction between a system of qubits is organized so that the system's Hamiltonian is similar to that of some quantum system of interest. Then the qubit system, first prepared in a certain initial state with relatively high energy, e.g., in an unentangled state described by Eq. (130), is let to evolve on its own. Due to the unavoidable dissipation due to interaction with environment, the system eventually relaxes to a final unentangled state of its qubits, which is then measured. From numerous runs of such experiment, outcome statistics may be revealed for various temperatures of the environment. Thus, at this approach (which is very close to the numerical modeling technique called *quantum annealing*), the interaction

⁷⁹ Note that qualifier “quantum” is important here, to distinguish this research direction from the option of *classical* adiabatic (or “reversible”) computation – see, e.g., SM Sec. 3.3 and references therein.

with environment is allowed to play a certain role in the system evolution, though every effort is made to reduce it, to allow qubit “quantumness” to make a substantial difference at least at the beginning of the relaxation process.

Generally speaking, adiabatic quantum computation may be used for performing any quantum algorithm, including number factoring.⁸⁰ Unfortunately, due to technical difficulties of the organization and precise control of long-range interaction in multi-qubit systems,⁸¹ the list of modeled systems is presently limited to a few simple 1D or 2D arrays described by the so-called *extended quantum Ising* (“spin-glass”) *model*⁸²

$$\hat{H} = -J \sum_{\{j,j'\}} \hat{\sigma}_z^{(j)} \hat{\sigma}_z^{(j')} - \sum_j h_j \hat{\sigma}_z^{(j)}, \quad (8.170)$$

where the curly bracket denotes the summation over pairs of close (though not necessarily closest) neighbors. Though Hamiltonian (170) is the traditional playground of phase transitions theory (see, e.g., SM Chapter 4), to the best of my knowledge there are not many practically valuable tasks that could be achieved by studying the statistics of its solutions. Moreover, even for this limited task, the speed of the best experimental adiabatic quantum “computer” with $N = 108$ qubits is still lower than that of a classical, off-the-shelf semiconductor processor (with a dollar cost lower by some 6 orders of magnitude), and no dramatic change of this comparison is predicted for realistic larger values of N .⁸³

There may be better prospects for another application of entangled qubit systems, namely for telecommunication cryptography.⁸⁴ The goal here is to replace the currently dominating classical encryption, based on the public-key RSA code mentioned above, that may be broken by factoring of very large numbers, by a quantum encryption that would be fundamentally unbreakable. The basis of this opportunity are the measurement postulate and the no-cloning theorem: if a message is carried out by a qubit such as a single photon, it is impossible for an eavesdropper (in cryptography, traditionally called *Eve*) to either measure or copy its faithfully, without also disturbing its state. However, as we have seen from the discussion of Fig. 7a, state *quasi*-cloning using entangled qubits is possible, so that the issue is far from being simple, especially if we want to use a publicly distributed quantum key, in some sense similar to the classical public key used at the RSA encryption.

Unfortunately, I do not have time/space to discuss various options for quantum encryption, but cannot help demonstrating how counter-intuitive they may be, on the famous example of the so-called *quantum teleportation* (Fig. 8).⁸⁵ Suppose that party A (in cryptography, traditionally called *Alice*) wants to send party B (*Bob*) the full information about the quantum state α of a qubit, unknown to either party. Instead of sending her qubit directly to Bob, Alice asks *him* to send *her* one qubit (β) of the pair of other qubits, prepared in a certain entangled state, for example in the singlet state (11):

⁸⁰ See, e.g., the experiments on factoring of number $143 = 13 \times 11$, using nuclear spin relaxation, by N. Xu *et al.*, *Phys. Rev. Lett.* **108**, 130501 (2012), though by the moment of this writing, their results remained controversial.

⁸¹ Due to the same reason, the implementation is so far limited to most scalable, Josephson-junction (flux) qubits – see, e.g., M. Johnson *et al.*, *Nature* **473**, 194 (2011).

⁸² For its classical version, see, e.g., SM Eq. (4.23) and its discussion.

⁸³ See S. Boxio *et al.*, *Nature Physics* **10**, 218 (2014) and T. Ronnow *et al.*, arXiv:1401.2910 [quant-ph].

⁸⁴ This field was pioneered in the 1970s by S. Wiesner.

⁸⁵ This procedure had been first suggested in 1993 by the same C. Bennett, and then repeatedly demonstrated experimentally – see, e.g., the recent paper by L. Steffen *et al.*, *Nature* **500**, 319 (2013), and literature therein.

$$|\beta\beta'\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle). \quad (8.171)$$

Using Eq. (125), the initial state of the whole 3-qubit system may be represented by the ket-vector

$$|\alpha\beta\beta'\rangle = (a_0|0\rangle + a_1|1\rangle)|\beta\beta'\rangle = \frac{a_0}{\sqrt{2}}|001\rangle - \frac{a_0}{\sqrt{2}}|010\rangle + \frac{a_1}{\sqrt{2}}|101\rangle - \frac{a_1}{\sqrt{2}}|111\rangle, \quad (8.172a)$$

which may be rewritten as a linear superposition,

$$\begin{aligned} |\alpha\beta\beta'\rangle &= \frac{1}{2}|\alpha\beta\rangle_s^+ (-a_1|0\rangle + a_0|1\rangle) + \frac{1}{2}|\alpha\beta\rangle_s^- (a_1|0\rangle + a_0|1\rangle) \\ &\quad + \frac{1}{2}|\alpha\beta\rangle_e^+ (-a_0|0\rangle + a_1|1\rangle) + \frac{1}{2}|\alpha\beta\rangle_e^- (-a_0|0\rangle - a_1|1\rangle), \end{aligned} \quad (8.172b)$$

of the following 4 states of qubit pair $\alpha\beta$:

$$|\alpha\beta\rangle_s^\pm \equiv \frac{1}{\sqrt{2}}(|00\rangle \pm |11\rangle), \quad |\alpha\beta\rangle_e^\pm \equiv \frac{1}{\sqrt{2}}(|01\rangle \pm |10\rangle). \quad (8.173)$$

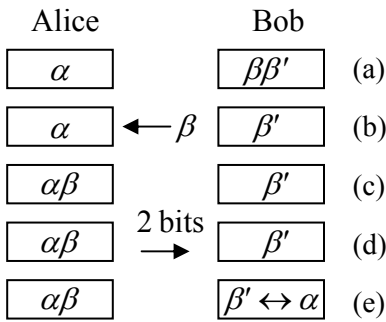


Fig. 8.8. Sequential stages of a quantum teleportation procedure: (a) the initial state with entangled qubits β and β' , (b) back transfer of qubit β' , (c) measurement of pair $\alpha\beta$, (d) forward transfer of 2 classical bits with the measurement result, and (e) the final state, with the state of qubit β' mirroring the initial state of qubit α .

After having received qubit β from Bob, Alice measures which of these 4 states does pair $\alpha\beta$ have. This may be achieved, for example, by measurement of one observable represented by operator $\hat{\sigma}_z^{(\alpha)}\hat{\sigma}_z^{(\beta)}$ and another one corresponding to $\hat{\sigma}_x^{(\alpha)}\hat{\sigma}_x^{(\beta)}$ - cf. Eq. (148).⁸⁶ The measured eigenvalue of the former operator enables distinguishing the couples of states (173) with different values of the lower index, while the latter measurement distinguishes the states with different upper indices.

Then Alice reports the result (that may be coded by just 2 classical bits) to Bob over a classical channel. Since the measurement places pair $\alpha\beta$ *definitely* in the corresponding state, the remaining Bob's bit β' is now *definitely* in the unentangled single-qubit state that is represented by the corresponding parentheses in Eq. (172b). Note that each of these parentheses contains both coefficients $a_{0,1}$, i.e. the whole information about the initial state of qubit α had initially. If Bob likes, he may now use appropriate single-qubit operations, similar to those discussed above, to move qubit β into the state *exactly* similar to the initial state of qubit α . (This fact does not violate the no-cloning theorem (159), because the measurement *has already* changed the state of α .) This is of course a “teleportation” only in

⁸⁶ All four states (172) are eigenstates of both these operators, so that the measurements do not affect each other and may be done in any order.

a very special sense of this rather ambiguous term, but a good example of the importance of qubit entanglement's preservation at their spatial transfer. For us, this is also a good primer for the forthcoming discussion of the *EPR paradox* and *Bell's inequalities* in Sec. 10.1.

Returning for a minute to practical quantum cryptography, since its two most common quantum key distribution protocols⁸⁷ require just a few simple quantum gates, whose experimental implementation is not a large obstacle, the main focus of the current effort is on decreasing single-photon dephasing in long optical fiber waveguides,⁸⁸ and hence increasing the maximum distance of quantum channels with sufficiently high qubit transfer fidelity. The recent progress was impressive, with demonstrated two lines (using either protocol) longer than 100 km,⁸⁹ and active plans for 560 km and 700 km landlines and several satellite-based systems. Let me hope that if not the author, then the reader of these notes will see this technology accepted for practical secure telecommunications.

8.6. Exercise problems

8.1. N electrons are placed in a 3D, spherically-symmetric quadratic potential $U(\mathbf{r}) = m\omega_0^2 r^2/2$. Neglecting the direct interaction of the electrons, find the ground-state energy of the system.

8.2. $N \gg 1$ indistinguishable, non-interacting quantum particles are placed in a hard-wall, rectangular box with sides a_x , a_y , and a_z . Calculate the ground-state energy of the system, and the average forces it exerts on each face of the box. Can we characterize the forces by certain pressure?

Hint: Consider separately the cases of bosons and fermions.

8.3. Prove that the singlet state, and each triplet state of a system of two indistinguishable spin- $1/2$ particles, are eigenstates of the operator of the scalar product $\mathbf{S}_1 \cdot \mathbf{S}_2$ of the spin vectors, and calculate the corresponding eigenvalues. Compare the results with the scalar product of two classical vectors of magnitude $\hbar/2$ each, being either parallel or antiparallel.

8.4. The interaction of two, indistinguishable spin- $1/2$ particles (that are otherwise free) has the form

$$\hat{H}_{\text{int}} = U(\mathbf{r}) + f(\mathbf{r}) \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2,$$

where $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ is the distance between the particles. Reduce the problem to two independent wave mechanical problems.

8.5. Two similar spin- $1/2$ particles, with the gyromagnetic ratio γ , localized at two points separated by distance a , interact via the field of their magnetic dipole moments. Calculate the eigenstates and eigenvalues of the system.

⁸⁷ BB84 suggested in 1984 by C. Bennett and G. Brassard, and EPRBE suggested in 1991 by A. Ekert. For details, see, e.g., either Sec. 12.6 in Nielsen and Chuang, or the review by N. Gisin *et al.*, *Rev. Mod. Phys.* **74**, 145 (2002).

⁸⁸ For their discussion see, e.g., EM Sec. 7.8.

⁸⁹ See P. Hiskett *et al.*, *New J. Phys.* **8**, 193 (2006), and R. Ursin *et al.*, *Nature Physics* **3**, 481 (2007).

8.6. In the simple case of just two similar spin-interacting particles, distinguishable by their spatial location, the famous *Heisenberg model* of ferromagnetism⁹⁰ is reduced to the following Hamiltonian:

$$\hat{H} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - \gamma\mathcal{B} \cdot (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2),$$

where J is the spin interaction constant, γ is the gyromagnetic ratio of each particle, and $\mathcal{B}$ is the external magnetic field. Find the stationary states and eigenenergies of this system for spin- $1/2$ particles.

8.7. Two distinguishable particles, both with spin $1/2$, but different gyromagnetic ratios γ_1 and γ_2 , are placed into external magnetic field $\mathcal{B}$. In addition, their spins interact as

$$\hat{H}_{\text{int}} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2.$$

Find the eigenstates and eigenenergies of the system.⁹¹

8.8. A system of 3 similar but distinguishable spin- $1/2$ particles is described by the following Hamiltonian:

$$\hat{H} = -J(\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_1),$$

where J is the spin interaction constant. Find the stationary states and eigenenergies of this system.

8.9. For a system of three distinguishable spins- $1/2$, find the joint eigenstates (and the corresponding eigenvalues) of operators S_z and S^2 , where

$$\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3$$

is the vector operator of the total spin of the system. Do the corresponding quantum numbers s and m_s obey Eqs. (5.197)?

8.10. Prove that Eq. (8.32) of the lecture notes indeed yields $E_g^{(1)} = (5/4)E_H$.

8.11. For a diluted gas on helium atom in their ground state, with n atoms per unit volume, on density n , calculate its:

- (i) electric susceptibility χ_e , and
- (ii) magnetic susceptibility χ_m ,

and compare the results.

8.12. Represent the operators of the total kinetic energy and the total orbital angular momentum of a system of two particles, with masses m_1 and m_2 , as combinations of terms describing their center-of-mass motion and relative motion.

8.13. Two particles, with masses m_1 and m_2 , interact as described by 3D potential

⁹⁰ For more discussion of this and other models of ferromagnetism and antiferromagnetism see SM Chapter 4.

⁹¹ For similar particles (in particular, with $\gamma_1 = \gamma_2$) the problem is reduced to the previous one.

$$U(\mathbf{r}_1, \mathbf{r}_2) = \frac{\kappa}{2} (\mathbf{r}_1 - \mathbf{r}_2)^2,$$

but otherwise are free to move. Calculate the energy spectrum and the degeneracy of each energy level of the system for the cases when the particles are:

- (i) distinguishable, and
- (ii) indistinguishable spin- $\frac{1}{2}$ fermions (such as electrons).

8.14. Two particles with similar masses m and charges q are free to move along a round, plane ring of radius R . In the limit of their strong Coulomb interaction, find the lowest eigenenergies of the system, and sketch the system of its energy levels.

8.15. Two similar 1D, spin- $\frac{1}{2}$ particles are attracting each other at contact:

$$U(x_1, x_2) = -w\delta(x_1 - x_2), \quad \text{with } w > 0,$$

but are otherwise free to move. Find the energy and the wavefunction of the ground state of the system.

Hint: Mind the possibility of various spin states of the particles.

8.16. Two indistinguishable, 1D, spin- $\frac{1}{2}$ particles in a triplet spin state are attracting each other at limited distance:

$$U(x_1, x_2) = \begin{cases} -U_0, & \text{for } |x_1 - x_2| < a/2, \\ 0, & \text{otherwise,} \end{cases} \quad \text{with } U_0 > 0,$$

but are otherwise free to move. How large should be a for the system to have at least one localized eigenstate? Relate the result to the solution of the previous problem.

8.17.* Two indistinguishable spin- $\frac{1}{2}$ particles are confined to move around a circle of radius R , and interact only at a very short distance $l = R\varphi = R(\varphi_1 - \varphi_2)$ between them, so that the interaction potential U may be well approximated with a delta-function of φ . Calculate their lowest ground states and their energy for the following two cases:

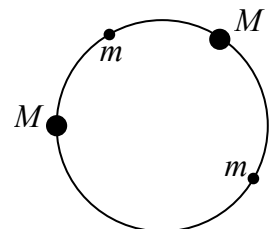
(i) “orbital” (spin-independent) interaction: $\hat{U} = w\delta(\varphi)$,

(ii) spin-spin interaction: $\hat{U} = -w\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2\delta(\varphi)$,

both with constant $w > 0$. Analyze the trends of your results in the limits $w \rightarrow 0$ and $w \rightarrow \infty$.

8.18. Low-energy spectrum of many diatomic molecules may be well described modeling the molecule as a system of two spinless particles connected with a light and elastic, but very stiff spring. Calculate the spectrum in this approximation.

8.19. Two particles of mass M , separated by two much lighter particles, of mass $m \ll M$, are placed on a ring of radius R – see Fig. on the right. The particles strongly repulse at contact, but otherwise each of them is free to move along the ring. Calculate the lower part of the energy spectrum of the system.



8.20.* Use the perturbation theory to calculate the contribution to the *hyperfine splitting* of the ground energy of the hydrogen atom, due to the interaction between spins of the nuclei (proton) and of the electron.

Hint: The proton's magnetic moment operator is described by Eq. (4.116), with a positive gyromagnetic factor $\gamma_p = g_p e / 2m_p \approx 2.675 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$, whose magnitude is much smaller than that of the electron ($|\gamma_e| \approx 1.761 \times 10^{11} \text{ s}^{-1} \text{ T}^{-1}$), due to a different g-factor, $g_p \approx 5.586$,⁹² and of course a much higher mass, $m_p \approx 1.673 \times 10^{-27} \text{ kg}$.

8.21. Discuss the factors $\pm 1/\sqrt{2}$ that participate in Eqs. (19) and (21), in terms of the Clebsch-Gordan coefficients discussed in Sec. 5.7.

8.22. Compose the simplest model Hamiltonians of the following systems, in terms of the second quantization formalism:

- (i) a system of two weakly coupled quantum wells, taking into account pair on-site interactions (additional energy J per each pair of particles in the same quantum well), and
- (ii) same for the motion in a periodic 1D potential, in the tight-binding limit.

8.23. For each of the Hamiltonians composed in the previous problem, derive the Heisenberg equations of motion for particle creation operators, for (i) bosons, and (ii) fermions.

8.24. Express the ket-vectors all possible Dirac states for the system of 3 indistinguishable

- (i) bosons, and
- (ii) fermions,

via those of their single-particle states.

8.25. Explain why the Hartree-Fock approximation (118), applied to the ^4He atom, gives “correct”⁹³ expression (31) for the ground singlet state, and correct Eqs. (44)-(45) (with the minus sign in the former relation) for the excited triplet state, but cannot describe result (44), with the plus sign, for the excited singlet state.

8.26. Find a time-independent Hamiltonian that may cause the qubit evolution described by Eq. (147). Discuss the result and its relation to the time-dependent Hamiltonian (6.86).

⁹² The anomalously large value of its g-factor may be qualitatively understood as a result of the three-quark structure of this particle. (The exact quantitative calculation of g_p still remains a challenge for quantum chromodynamics.)

⁹³ Correct in the sense of the 1st order of the perturbation theory.

Chapter 9. Introduction to Relativistic Quantum Mechanics

This chapter gives a brief introduction to relativistic quantum mechanics. It starts with a discussion of the basic elements of the quantum theory of electromagnetic field (quantum electrodynamics, QED), including the quantization scheme, photon statistics, radiative atomic transitions, the spontaneous and stimulated radiation, and the so-called cavity QED. Then I will briefly review the relativistic quantum theory of particles with nonvanishing rest mass, notably Dirac' theory of spin- $\frac{1}{2}$ particles, and mark the point of entry into the most complete relativistic quantum theory – the quantum field theory, QFT – which is beyond the scope of these notes.¹

9.1. Electromagnetic field quantization

Classical mechanics tells us² that the relativistic relation between momentum $\mathbf{p}$ and energy E of a free particle with rest mass m may be simplified in two limits, nonrelativistic and ultrarelativistic:

Free
particle's
relativistic
energy

$$E = [(pc)^2 + (mc^2)^2]^{1/2} \rightarrow \begin{cases} mc^2 + p^2 / 2m, & \text{for } p \ll mc, \\ pc, & \text{for } p \gg mc. \end{cases} \quad (9.1)$$

In both limits, the transfer from classical to quantum mechanics is easier than in the arbitrary case. Since all the previous part of this course was committed to the first, non-relativistic limit, I will now jump to a brief discussion of the ultrarelativistic limit $p \gg mc$, for a particular but very important system - the electromagnetic field. Since the excitations of this field, called *photons*, are currently believed to have zero rest mass m ,³ the ultrarelativistic limit is valid for any photon energy E , and the quantization scheme is rather straightforward.

As usual, the quantization has to be based on the classical theory of the system, in this case the Maxwell equations. As the simplest case, let us consider electromagnetic field in a free-space volume limited by ideal walls that reflect incident waves perfectly.⁴ Inside the volume, the Maxwell equations may be reduced to a simple wave equation⁵ for electric field

$$\nabla^2 \mathcal{E} - \frac{1}{c^2} \frac{\partial^2 \mathcal{E}}{\partial t^2} = 0, \quad (9.2)$$

and an absolutely similar equation for magnetic field $\mathcal{B}$. We may look for the general solution of Eq. (2) in the variable-separating form

¹ Note that some material of this chapter is frequently taught as a part of the QFT. I will focus on a few most important results that may be obtained without starting heavy QFT engines.

² See, e.g., EM Chapter 9.

³ By now this fact has been verified experimentally with an accuracy of at least $\sim 10^{-22} m_e$ – see S. Eidelman *et al.*, *Phys. Lett. B* **592**, 1 (2004).

⁴ In the case of finite energy absorption in the walls, or in the wave propagation media (say, described by complex constants ε and μ), the system would not be energy-conserving (Hamiltonian), i.e. would interact with the dissipative environment. Specific cases of such interaction will be considered in Sections 2 and 3 below.

⁵ See, e.g., EM Eq. (7.3), for the particular case $\varepsilon = \varepsilon_0$, $\mu = \mu_0$, $v^2 \equiv 1/\varepsilon\mu = 1/\varepsilon_0\mu_0 \equiv c^2$.

$$\mathcal{E}(\mathbf{r}, t) = \sum_j p_j(t) \mathbf{e}_j(\mathbf{r}). \quad (9.3)$$

Physically, each term of this sum is a standing wave whose spatial distribution and polarization (“mode”) is described by vector function $\mathbf{e}_j(\mathbf{r})$, and the temporal dynamics, by function $p_j(t)$. Plugging an arbitrary term of this sum into Eq. (2), and separating variables exactly as we did, e.g., for the Schrödinger equation in Sec. 1.4, we get

$$\frac{\nabla^2 \mathbf{e}_j}{\mathbf{e}_j} = \frac{1}{c^2} \frac{\ddot{p}_j}{p_j} = \text{const} \equiv -k_j^2, \quad (9.4)$$

so that the spatial distribution of the mode satisfies the *3D Helmholtz equation*:

$$\nabla^2 \mathbf{e}_j + k_j^2 \mathbf{e}_j = 0. \quad (9.5)$$

Equation
for spatial
distribution

The set of solutions of this equation, with appropriate boundary conditions, determines the set of functions $\mathbf{e}_j$ and simultaneously the spectrum of wave number moduli k_j . The latter values determine mode eigenfrequencies, following from Eq. (4):

$$\ddot{p}_j + \omega_j^2 p_j = 0, \quad \text{with } \omega_j \equiv k_j c. \quad (9.6)$$

There is a big philosophical difference between the approaches to equations (5) and (6), despite their single origin (4). The first (Helmholtz) equation may be rather difficult to solve in realistic geometries,⁶ but it remains intact in quantum theory, with the scalar components of vector functions $\mathbf{e}_j(\mathbf{r})$ still treated (at each point $\mathbf{r}$) as *c*-numbers. In contrast, Eq. (6) is readily solvable (giving sinusoidal oscillations with frequency ω_j), but this is exactly where we can make a transfer to quantum mechanics, because we already know how to quantize a mechanical 1D harmonic oscillator that obeys, in classics, the same equation.

As usual, we need to start with the appropriate Hamiltonian corresponding to the classical Hamiltonian function H of the proper set of generalized coordinates and momenta. The electromagnetic field’s Hamiltonian function (that in this case coincides with field’s energy) is⁷

$$H = \int d^3 r \left(\frac{\varepsilon_0 \mathcal{E}^2}{2} + \frac{\mathcal{B}^2}{2\mu_0} \right). \quad (9.7)$$

Let us represent the magnetic field in a form similar to Eq. (3),

$$\mathcal{B}(\mathbf{r}, t) = - \sum_j \omega_j q_j(t) \mathbf{b}_j(\mathbf{r}). \quad (9.8)$$

Since, according to the Maxwell equations, in our case the magnetic field satisfies the equation similar to Eq. (2), the time-dependent amplitude q_j of each of its modes obey the equation similar to Eq. (6), i.e. also changes in time sinusoidally, with the same frequency ω_j . Plugging Eqs. (3) and (8) into Eq. (7), we may recast it as

⁶ See, e.g., various problems discussed in EM Chapter 7, especially in Sec. 7.9.

⁷ See, e.g., EM Sec. 9.8, in particular, Eq. (9.225). I am using SI units, with $\varepsilon_0 \mu_0 \equiv c^{-2}$; in the Gaussian units, coefficients ε_0 and μ_0 disappear, but there is an additional common factor $1/4\pi$ in the equation for energy. If we modify the normalization conditions accordingly, all the subsequent results look similar in any system of units.

$$H = \sum_j \frac{p_j^2}{2} \int \varepsilon_0 e_j^2(\mathbf{r}) d^3r + \frac{\omega_j^2 q_j^2}{2} \int \frac{1}{\mu_0} b_j^2(\mathbf{r}) d^3r, \quad (9.9)$$

Since the distribution of constant factors between two multiplication operands in each term of Eq. (3) is arbitrary, we may fix it by requiring the first integral in Eq. (9) to equal 1. It is straightforward to check that according to the Maxwell equations, which give a specific relation between vectors $\mathcal{E}$ and $\mathcal{B}$,⁸ this normalization makes the second integral in Eq. (9) equal 1 as well, and Eq. (9) becomes

$$H = \sum_j H_j, \quad H_j = \frac{p_j^2}{2} + \frac{\omega_j^2 q_j^2}{2}. \quad (9.10)$$

Now we can carry out the standard quantization procedure, namely declare H_j , p_j , and q_j the quantum-mechanical operators related exactly as in Eq. (10),

Electro-
magnetic
mode's
Hamiltonian

$$\hat{H}_j = \frac{\hat{p}_j^2}{2} + \frac{\omega_j^2 \hat{q}_j^2}{2}. \quad (9.11)$$

we see that this Hamiltonian coincides with that of a 1D harmonic oscillator with the mass m_j formally equal to 1,⁹ and the eigenfrequency equal to ω_j . Now, in order to plug Eq. (11) into Eq. (4.199) for the time evolution of Heisenberg-picture operators $\hat{p}_j$ and $\hat{q}_j$, we need to know the commutation relation between these operators. For that, returning to the classical case, let us calculate the Poisson bracket (4.204) for “functions” $A = q_{j'}$ and $B = p_{j''}$:

$$\{q_{j'}, p_{j''}\} \equiv \sum_j \left(\frac{\partial q_{j'}}{\partial p_j} \frac{\partial p_{j''}}{\partial q_j} - \frac{\partial q_{j'}}{\partial q_j} \frac{\partial p_{j''}}{\partial p_j} \right). \quad (9.12a)$$

Since in the classical Hamiltonian mechanics, all generalized coordinates q_j and momenta p_j have to be considered independent arguments of H , only one term (with $j = j' = j''$) in only one sum (12) (with $j' = j''$), gives a nonvanishing value (-1), so that

$$\{q_{j'}, p_{j''}\} = -\delta_{jj''}. \quad (9.12b)$$

Hence, according to the general quantization rule (4.205), the commutation relation of the operators corresponding to $q_{j'}$ and $p_{j''}$ is

$$[\hat{q}_{j'}, \hat{p}_{j''}] = i\hbar \delta_{jj''}, \quad (9.13)$$

i.e. is exactly the same as for the usual Cartesian components of the radius-vector and momentum of a mechanical particle.

As the reader already knows, Eqs. (11) and (13) open for us several alternative ways to proceed:

⁸ See, e.g., EM Eq. (7.6).

⁹ With different normalizations of functions $\mathbf{e}_j(\mathbf{r})$ and $\mathbf{b}_j(\mathbf{r})$, we could readily arrange any value of m_j , and the choice corresponding to $m_j = 1$ is the best one just for the notation simplicity. Note also that I am using notation q_j instead of x_j for the generalized coordinate of the field oscillator, in order to emphasize the difference between the former variable, defined by Eq. (8), and one of the Cartesian coordinates, i.e. one of arguments of c -number functions $\mathbf{e}$ and $\mathbf{b}$.

(i) Use the Schrödinger-picture wave mechanics based on wavefunctions $\Psi_j(q_j, t)$. As we know from Sec. 2.10, this way is inconvenient for most tasks, because eigenfunctions of the harmonic oscillator are rather clumsy.

(ii) A substantially better way is to write the equations of time evolution of the Heisenberg-picture operators $\hat{q}_j(t)$ and $\hat{p}_j(t)$.

(iii) An even more convenient approach is to use equations similar to Eqs. (5.99) to decompose operators $\hat{q}_j(t)$ and $\hat{p}_j(t)$ into the creation-annihilation operators $\hat{a}_j^\dagger$ and $\hat{a}_j$, and work with these operators using either the Schrödinger or the Heisenberg picture, depending on the problem.

I will mostly use the last route. Replacing m with $m_j \equiv 1$, and ω_0 with ω_j , the last forms of Eqs. (5.98) become

$$\hat{a}_j = \left(\frac{\omega_j}{2\hbar} \right)^{1/2} \left(\hat{q}_j + i \frac{\hat{p}_j}{\omega_j} \right), \quad \hat{a}_j^\dagger = \left(\frac{\omega_j}{2\hbar} \right)^{1/2} \left(\hat{q}_j - i \frac{\hat{p}_j}{\omega_j} \right), \quad (9.14)$$

and due to Eq. (13), the creation-annihilation operators obey the commutation similar to Eq.(5.101),

$$[\hat{a}_j, \hat{a}_{j'}^\dagger] = \hat{I} \delta_{jj'}, \quad (9.15)$$

so that, according to Eqs. (3) and (8), the quantum-mechanical operators corresponding to the electric and magnetic fields are

$$\hat{\mathcal{E}}(\mathbf{r}, t) = i \sum_j \left(\frac{\hbar \omega_j}{2} \right)^{1/2} \mathbf{e}_j(\mathbf{r}) \left(\hat{a}_j^\dagger - \hat{a}_j \right), \quad (9.16a)$$

$$\hat{\mathcal{B}}(\mathbf{r}, t) = \sum_j \left(\frac{\hbar \omega_j}{2} \right)^{1/2} \mathbf{b}_j(\mathbf{r}) \left(\hat{a}_j^\dagger + \hat{a}_j \right), \quad (9.16b)$$

Electro-
magnetic
fields'
operators

and Eq. (11) for j^{th} mode's Hamiltonian becomes

$$\hat{H}_j = \hbar \omega_j \left(\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2} \hat{I} \right) = \hbar \omega_j \left(\hat{n}_j + \frac{1}{2} \hat{I} \right), \quad \text{with } \hat{n}_j \equiv \hat{a}_j^\dagger \hat{a}_j, \quad (9.17)$$

absolutely similar to Eq. (5.505) for a mechanical oscillator.

Now comes a very important conceptual step. From Sec. 5.4 we know that eigenstates (Fock states n_j) of Hamiltonian (17) have energies

$$E_j = \hbar \omega_j \left(n_j + \frac{1}{2} \right), \quad n_j = 0, 1, 2, \dots \quad (9.18)$$

Electro-
magnetic
mode's
eigen-
energies

and, according to Eq. (5.115), operators $\hat{a}_j^\dagger$ and $\hat{a}_j$ act on the eigenkets of these states as

$$\hat{a}_j |n_j\rangle = (n_j)^{1/2} |n_j - 1\rangle, \quad \hat{a}_j^\dagger |n_j\rangle = (n_j + 1)^{1/2} |n_j + 1\rangle, \quad (9.19)$$

regardless of the quantum states of other modes (frequently called *field oscillators*). These rules coincide with definitions (8.56) and (8.60) of bosonic creation-annihilation operators, and hence their action may be considered as the creation/annihilation of certain bosons. Such a “particle” (actually, an *excitation* of an electromagnetic field oscillator) is exactly what is, strictly speaking, called a *photon*. Note immediately that according to Eq. (16), such an excitation does not change the spatial distribution of the j^{th} mode of the field. So, such a “global” photon is an excitation created simultaneously at all points of the field confinement region.

If this picture is too contrary to the intuitive image of a particle, please recall that we had a similar situation in Chapter 2 with eigenstates of the nonrelativistic Schrödinger equation: the represented a standing de Broglie wave existing simultaneously in all points of the particle confinement region. The (partial :-) reconciliation with the classical picture of a moving particle might be obtained by using the linear superposition principle to assemble a quasi-localized wave packet of sinusoidal waves, with close wave numbers. Very similarly, we may form a quasi-localized wave packet using a linear superposition of the “global” photons with close values of k_j (and hence ω_j). An additional simplification here is that since the dispersion relation for electromagnetic waves is linear:

$$\frac{\partial \omega_j}{\partial k_j} = c = \text{const}, \quad \text{i.e.} \quad \frac{\partial^2 \omega_j}{\partial k_j^2} = 0, \quad (9.20)$$

so that, according to Eq. (2.39a), the electromagnetic wave packets (localized photons) do not spread out during their propagation.

The next important conceptual issue is that of the ground-state energy. Equation (18) implies that the total ground-state (i.e., the lowest) energy of the field is

$$E_g = \sum_j (E_g)_j = \sum_j \frac{\hbar \omega_j}{2}. \quad (9.21)$$

Ground-
state
energy
of the field

This sum diverges at high frequencies for any realistic any realistic model of the field-confining volume – either infinite or not. Any attempt to dismiss this paradox by declaring the zero-point energy unobservable and hence non-existing fails due to several experimental facts.

First of all, the ground-state “fluctuations” (sometimes called “quantum noise”) can be directly observed – see Sec. 7.5 and in particular the literature cited therein. Second, there is the *Casimir effect*.¹⁰ The simplest manifestation of the effect involves two parallel plates separated by a vacuum gap of thickness $d \ll A^{1/2}$, where A is the plate area (Fig. 1). Rather counter-intuitively, the plates attract each other with a force proportional to area A , and rapidly increasing at the decrease of gap d .



Fig. 9.1. Generic geometry of the Casimir effect manifestation.

¹⁰ It was predicted in 1948 by H. Casimir and D. Polder, and confirmed semi-quantitatively in experiments by M. Sparnaay, *Nature* **180**, 334 (1957) and others. A decisive error bar reduction (to about ~5%), providing a quantitative confirmation of the Casimir formula (23), was achieved by S. Lamoreaux, *Phys. Rev. Lett.* **78**, 5 (1997) and U. Mohideen and A. Roy, *Phys. Rev. Lett.* **81**, 004549 (1998).

The effect's explanation is that the energy of each the electromagnetic field mode, including the ground-state energy, is intimately related with the average pressure,

$$\langle P_j \rangle = -\frac{\partial E_j}{\partial V}, \quad (9.22)$$

exerted by the field on the walls constraining it to volume V . While its pressure on the external surfaces on the plates is due to sum (21) over all free-space modes, with arbitrary values of k_z (the z -component of the wave vector $\mathbf{k}_j$), between the plates the spectrum of k_z is limited to multiples of π/d , so that the pressure on the internal surfaces is lower. The net pressure may be found as the sum of contributions (22) from all “missing” low-frequency modes in the gap. The calculations are rather simple if the plates are made of an ideal conductor (which provides boundary conditions $E_n = 0$ and $B_\tau = 0$ on the plate surfaces), and the result is¹¹

$$\langle P \rangle = \sum_j \langle P_j \rangle = -\frac{\pi^2 \hbar c}{240 d^4}. \quad (9.23) \quad \text{Casimir effect}$$

Note that for this summation, the high-frequency divergence of Eq. (21) at high frequencies is not important, because it participates in the forces exerted on all surfaces of each plate, and hence cancels out from the net pressure. In this way, the Casimir effect not only gives a confirmation of Eq. (21), but also teaches us an important lesson how to deal with the divergence of this sum at $\omega_j \rightarrow \infty$: just get accustomed to the idea that the divergence exists and ignore the fact while you can. However, for more complex tasks of quantum electrodynamics (and quantum theory of any other field) this approach becomes impossible, and then more complex, *renormalization* techniques become necessary. For their study, I have to refer the reader to a quantum field theory course – see the literature cited in the end of this chapter.

9.2. Photon statistics

As a matter of principle, the Casimir effect may be used to measure not only the free-space electromagnetic field, but also that arriving from local sources - lasers, etc. However, usually this is done by simpler detectors in which the absorption of a photon by a single atom leads to its ionization. This ionization, i.e. emission of a free electron, triggers a chain reaction (i.e., an electric discharge in a Geiger-type counter) that may readily be registered by appropriate electronic circuitry. In order to discuss the statistics of such *photon counts*, it is sufficient to consider the field interaction with just one,

¹¹ For realistic metals, the reduction of d below $\sim 1 \mu\text{m}$ causes significant deviations from this simple model, and hence from Eq. (23). The reason is that at the important frequencies $\omega \sim c/d$, the depth of field penetration into the metal (see, e.g., EM Secs. 2.1 and 6.2) becomes comparable with d , and a theory of the Casimir effect has to involve a certain model of field penetration. (It is curious that in-depth analyses of this problem, pioneered in 1956 by E. Lifshitz, have revealed a deep relation between the Casimir effect and the long-range London dispersion forces which were the subject of Problems 3.7, 5.10 and 6.8 – for a review see, e.g., either I. Dzhyaloshinskii *et al.*, *Sov. Phys. Uspekhi* **4**, 153 (1961), or K. Milton, *The Casimir Effect*, World Scientific, 2001.) Recent experiments in the 100 nm – 2 μm range of distances d , with accuracy better than 1%, allowed even to distinguish the difference between alternative approximate models of field penetration – see D. Garcia-Sanchez *et al.*, *Phys. Rev. Lett.* **109**, 027202 (2012).

“trigger” atom. The atom’s size a is typically much smaller than the radiation wave length $\lambda_j = 2\pi/k_j$, so that their interaction is adequately described in the electric dipole approximation,

$$\hat{H}_{\text{int}} = -\hat{\mathcal{E}} \cdot \hat{\mathbf{d}}, \quad (9.24)$$

where $\hat{\mathbf{d}}$ is the dipole moment’s operator.¹² In Sec. 6.5 we have already developed an approach suitable for the analysis of this problem, based on the Golden Rule – see Fig. 6.14 and Eq. (6.152).¹³ In our current case, we may associate system b with the “trigger atom” (whose ionized states form a continuum spectrum), and hence operator $\hat{\mathbf{d}}$ in Eq. (24) with operand $\hat{B}$ in Eq. (6.148), while the electromagnetic field is represented by system a , and its electric field operator $\hat{\mathcal{E}}$ is associated with operand $\hat{A}$ in that relation. Let us assume, for simplicity, that our field consists of only one mode $\mathbf{e}_j(\mathbf{r})$.¹⁴ Then we can keep only one term in Eq. (16a), and drop index j , so that Eq. (6.152), for the transition from certain initial state ini to a final state fin may be rewritten as

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar} \left| \langle fin | \hat{\mathcal{E}}(\mathbf{r}, t) | ini \rangle \right|^2 \left| \langle fin | \hat{\mathbf{d}} \cdot \mathbf{n}_e | ini \rangle \right|^2 \rho_f \\ &= \frac{2\pi}{\hbar} \frac{\hbar\omega}{2} \left| \langle fin | \left(\hat{a}^\dagger - \hat{a} \right) e(\mathbf{r}) | ini \rangle \right|^2 \left| \langle fin | \mathbf{r} \cdot \mathbf{n}_e | ini \rangle \right|^2 \rho_f, \end{aligned} \quad (9.25)$$

where $e(\mathbf{r})$ is the local magnitude of vector $\mathbf{e}(\mathbf{r})$, and $\mathbf{n}_e \equiv \mathbf{e}(\mathbf{r})/e(\mathbf{r})$ is its local direction.¹⁵ As a reminder, in the Heisenberg picture of quantum mechanics, the initial and final states are time-independent, while the creation-annihilation operators are functions of time. In this Golden Rule formula, as in any perturbation result, this time dependence has to be calculated ignoring the perturbation – in this case the field-atom interaction. For the field’s creation-annihilation operators, this dependence coincides with that of the usual 1D oscillator – see Eq. (5.171), in which ω_0 should be now replaced with ω :

$$\hat{a}(t) = \hat{a}(0)e^{-i\omega t}, \quad \hat{a}^\dagger(t) = \hat{a}^\dagger(0)e^{+i\omega t}. \quad (9.26)$$

Hence Eq. (9.25) becomes

$$\Gamma = \pi\omega \left| \langle fin | \left(\hat{a}^\dagger(0)e^{i\omega t} - \hat{a}(0)e^{-i\omega t} \right) e(\mathbf{r}) | ini \rangle \right|^2 \left| \langle fin | \hat{\mathbf{d}}(t) \cdot \mathbf{n}_e | ini \rangle \right|^2 \rho_{fin}. \quad (9.27a)$$

Now let us multiply the first bra-ket by $\exp\{i\omega t\}$, and the second one by $\exp\{-i\omega t\}$:

¹² As a reminder: this relation, with the single-particle expression $\mathbf{d} = q\mathbf{r}$, has already been used several times – see, e.g., Eqs. (6.32) and (6.149). In contrast to the former of those cases, now we have to account for the quantum nature of the electromagnetic field $\mathcal{E}$, so in Eq. (24) it is represented by the (vector) operator (16a).

¹³ Please note that (as was promised) we have gradually slipped to the analysis of open, irreversible systems, with the detector(s) playing the role of a continuous-spectrum environment for the quantized electromagnetic field.

¹⁴ In a multimode field, the modes are typically incoherent, so that the total transition rate may be calculated as the sum of the partial rates of each mode – as we will do for a certain case below.

¹⁵ By the way, this expression shows that for the single-particle transitions from the ground state to n^{th} Fock state, the absorption rate is indeed proportional to the *oscillator strength* $f_n \equiv (2m/\hbar^2)(E_n - E_0) |\langle n|x|0 \rangle|^2$ of the transition, where x is particle’s coordinate in the direction of the external field. As was discussed in Chapter 5, the strengths obey the Thomas-Reiche-Kuhn sum rule $\sum_n f_n = 1$.

$$\Gamma = \pi\omega \left| \langle fin | \left(\hat{a}^\dagger(0)e^{2i\omega t} - \hat{a}(0) \right) e(\mathbf{r}) | ini \rangle \right|^2 \left| \langle fin | \hat{\mathbf{d}}(t) \cdot \mathbf{n}_e e^{-i\omega t} | ini \rangle \right|^2 \rho_{fin}. \quad (9.27b)$$

The physical sense of this, mathematically trivial, operation is that at resonant photon absorption, only the *annihilation* operator gives a significant time-averaged contribution to the first bra-ket matrix element. (Similarly, according to Eq. (4.199), the Heisenberg operator of the dipole moment, corresponding to the *increase* of atom's energy, has only the Fourier components that differ from ω only by $\sim \Gamma \ll \omega$, so that its time dependence compensates the additional factor in the second bra-ket of Eq. (27b), so that this bra-ket is also frequency-independent and has a substantial time average.) Hence, we can neglect the fast-evolving term in the first bra-ket whose average over time interval $\sim 1/\Gamma$ is very close to zero.¹⁶

Now let us assume that we use the same detector, characterized by the same second bra-ket and the same state density ρ_{fin} , for measurement of various electromagnetic fields - or just the same field at different points $\mathbf{r}$. Then we are only interested in the behavior of the first, field-related factor, and may write

$$\Gamma \propto \left| \langle fin | \hat{a}e(\mathbf{r}) | ini \rangle \right|^2 = \langle fin | \hat{a}e(\mathbf{r}) | ini \rangle \langle fin | \hat{a}e(\mathbf{r}) | ini \rangle^* = \langle ini | \hat{a}^\dagger e^*(\mathbf{r}) | fin \rangle \langle fin | \hat{a}e(\mathbf{r}) | ini \rangle, \quad (9.28)$$

where the creation-annihilation operators are assumed to be taken in the initial moment (i.e., in the Schrödinger picture), and the initial and final states are those of the field alone. As we know, any 1D harmonic oscillator (and hence the electromagnetic field oscillator) has many equidistant levels, so even if it initially was in a certain state, it may undergo be several coherent transitions to different finite Fock states. If we want to calculate the total rate, we may sum the transition rates into all finite states. Then, since these states form a full and orthonormal set, we may use the closure condition (4.44) to get

$$\Gamma \propto \sum_{fin} \langle ini | \hat{a}^\dagger e^*(\mathbf{r}) | fin \rangle \langle fin | \hat{a}e(\mathbf{r}) | ini \rangle = \langle ini | \hat{a}^\dagger \hat{a} | ini \rangle e^*(\mathbf{r})e(\mathbf{r}) = \langle n \rangle_{ini} |e(\mathbf{r})|^2. \quad (9.29)$$

Photon
counting
rate

Let us apply this formula to several possible quantum states of the field mode.

(i) First, as a sanity check, the ground initial state ($n = 0$) gives no photon counts at all. The interpretation is easy: the ground state cannot emit a photon that would trigger an atom in the counter. Again, this does not mean that the ground-state motion is not observable (if you still think so, please review the Casimir effect discussion in the last section), just that it cannot ionize an atom in the detector – because it does not have any *spare* energy for doing that.

(ii) All other coherent states (Fock, Glauber, squeezed, etc.) of the field oscillator give the same counting rate, provided that their $\langle n \rangle$ is the same. This result may be less evident if we apply Eq. (29) to an interference of two light beams from the same source (say, in the double-slit or the Bragg-scattering configurations). In this case we may present the spatial distribution of the field as a sum

$$e(\mathbf{r}) = e_1(\mathbf{r}) + e_2(\mathbf{r}). \quad (9.30)$$

Here each term describes one possible wave path, so that the field product in Eq. (29) may be a rapidly changing function of the detector position. For this configuration, our result (29) means that the

¹⁶ This is essentially the same rotating wave approximation (RWA) which was already used in Sec. 6.3 – see the transition from Eq. (6.90) to the first of Eqs. (6.94).

interference pattern (and its contrast) are independent of the particular state of the electromagnetic field's mode.

(iii) Surprisingly, the last statement is also valid for a classical mixture of the different eigenstates of the same field mode, for example for its thermal-equilibrium state. Indeed, in this case we need to average Eq. (29) over the corresponding classical ensemble, but it would only result in a different meaning of averaging n in that equation; the field part describing the interference pattern is not affected.

The last result may look a bit counter-intuitive, because common sense tells us that the stochasticity associated with thermal equilibrium has to suppress the interference pattern contrast. These expectations are (partly :-) justified, because a typical thermal source of radiation produces many field modes j , rather than one mode we have analyzed. These modes may have different wave numbers k_j and hence different field distribution functions $\mathbf{e}_j(\mathbf{r})$, resulting in shifted interference patterns. Their summation would indeed smear the interference, suppressing its contrast.

So the use of a single photon detector is not a suitable way to distinguish different quantum states of an electromagnetic field modes. This task, however, may be achieved using the photon counting correlation technique shown in Fig. 2.¹⁷

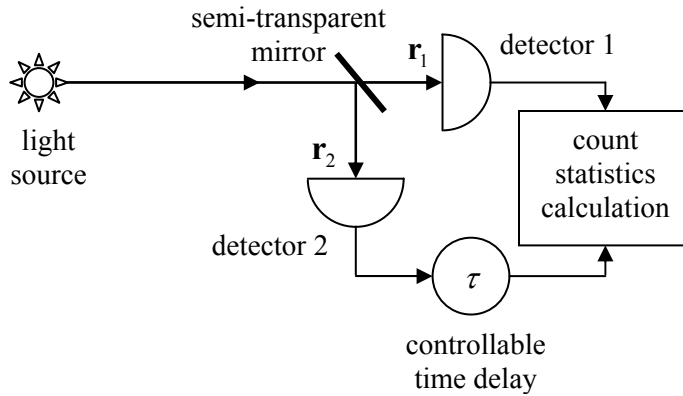


Fig. 9.2. Photon counting correlation measurements. (The intensities of the split beams should be comparable, but not necessarily equal.)

In this experiment, the counter rate correlation may be characterized by the so-called *second-order correlation function*¹⁸ of the counting rates,

$$g^{(2)}(\tau) \equiv \frac{\langle \Gamma_1(t) \Gamma_2(t - \tau) \rangle}{\langle \Gamma_1(t) \rangle \langle \Gamma_2(t) \rangle}, \quad (9.31)$$

Second-order correlation function: definition

¹⁷ It was pioneered as early as in the mid-1950s (i.e. before the advent of lasers!), by R. Hanbury Brown and R. Twiss. Their first experiment was also remarkable for the rather unusual light source they used – star Sirius! (It was a part of an attempt to improve astrophysics interferometry techniques.)

¹⁸ The reader may be interested what is the *first-order* correlation function. It is usually defined as

$$g^{(1)}(\tau) \equiv \left\langle \hat{\mathcal{E}}(\mathbf{r}_1, t) \hat{\mathcal{E}}^\dagger(\mathbf{r}_2, t - \tau) \right\rangle / \left[\left\langle \hat{\mathcal{E}}(\mathbf{r}_1, t) \hat{\mathcal{E}}^\dagger(\mathbf{r}_1, t) \right\rangle \left\langle \hat{\mathcal{E}}(\mathbf{r}_2, t) \hat{\mathcal{E}}^\dagger(\mathbf{r}_2, t) \right\rangle \right]^{1/2}.$$

In the single-mode case, and the rotating-wave approximation, the function is proportional to the c -number product $\mathbf{e}(\mathbf{r}_1) \mathbf{e}^*(\mathbf{r}_2)$, with all creation-annihilation operators cancelled, i.e. is suitable for characterizing interference patterns (30), but not the quantum state of the electromagnetic field.

where the averaging may be carried out either over many similar experiments, or over time t , due to the ergodicity of the experiment (with a stationary light source). Using the normalized correlation function (31) is very convenient, because characteristics of the detectors and beam splitter drop out from this fraction.

Very unexpectedly for the mid-1950s, Hanbury Brown and Twiss discovered that the correlation function depends on time delay τ in the way shown schematically by the solid line in Fig. 3. It is evident from Eq. (31) that if the counting events are completely independent, $g^{(2)}(\tau)$ should be equal 1 – which is always the case in the limit $\tau \rightarrow \infty$. Hence, the observed behavior at $\tau \rightarrow 0$ corresponds to the *positive* correlation of detector counts at small time delays, i.e. to a *higher* probability of the nearly-simultaneous arrival of photons to both counters. This effect is called the *photon bunching*.

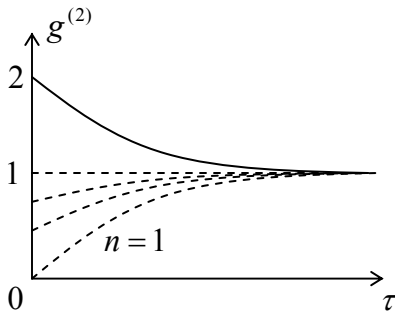


Fig. 9.3. Photon bunching (solid line) and antibunching for various n (dashed lines). The lines approach level $g^{(2)} = 1$ at $\tau \rightarrow \infty$ (on the time scale depending on the light source).

Let us use our simple single-mode model to analyze this experiment. Now the elementary quantum process, characterized by the nominator of Eq. (31), is the correlated triggering of two counters, at two spatial-temporal points $\{\mathbf{r}_1, t\}$ and $\{\mathbf{r}_2, t - \tau\}$, by the same field mode, so that we need to make the following replacement, in the first of Eqs. (25):

$$\hat{\mathcal{E}}(\mathbf{r}, t) \rightarrow \text{const} \times \hat{\mathcal{E}}(\mathbf{r}_1, t) \hat{\mathcal{E}}(\mathbf{r}_2, t - \tau). \quad (9.32)$$

Repeating all the manipulations done in the single-counter case, we get

$$\langle \Gamma_1(t) \Gamma_2(t - \tau) \rangle \propto \langle ini | \hat{a}^\dagger(t) \hat{a}(t - \tau) \hat{a}^\dagger(t - \tau) \hat{a}(t) | ini \rangle e^* (\mathbf{r}_1) e^* (\mathbf{r}_2) e(\mathbf{r}_1) e(\mathbf{r}_2). \quad (9.33)$$

Plugging this expression, as well as Eq. (29) for single-counter rates, into Eq. (31), we see that the field distribution factors (as well as the detector-specific bra-kets and the density of states ρ_{fin}) cancel, giving a very simple final expression

$$g^{(2)}(\tau) = \frac{\langle \hat{a}^\dagger(t) \hat{a}^\dagger(t - \tau) \hat{a}(t - \tau) \hat{a}(t) \rangle}{\langle \hat{a}^\dagger(t) \hat{a}(t) \rangle^2}, \quad (9.34)$$

where the averaging should be carried out, as before, over the initial state of the field. Still, the calculation of this expression for arbitrary τ may be quite complex, because the relaxation of the correlation function to the asymptotic value $g^{(2)}(\infty)$ in many cases is due to the interaction of the light source with environment, and hence requires the open-system techniques which were discussed in Chapter 7. However, the zero-delay value $g^{(2)}(0)$ may be calculated in a straightforward way, because the time arguments of all operators are equal, so that we may write

Zero-
delay
correlation

$$g^{(2)}(0) = \frac{\langle \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} \rangle}{\langle \hat{a}^\dagger \hat{a} \rangle^2}. \quad (9.35)$$

Let us evaluate this ratio for the simplest states of the field. (Remember, we are working in the Schrödinger picture now.)

(i) n^{th} Fock state. In this case, it is convenient to act by the annihilation operators upon the ket-vectors, and by the creation operators, upon the bra-vectors, using Eq. (19):

Photon
anti-
bunching

$$g^{(2)}(0) = \frac{\langle n | \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} | n \rangle}{\langle n | \hat{a}^\dagger \hat{a} | n \rangle^2} = \frac{\langle n-2 | [n(n-1)]^{1/2} [n(n-1)]^{1/2} | n-2 \rangle}{\langle n-1 | n^{1/2} n^{1/2} | n-1 \rangle^2} = \frac{n(n-1)}{n^2} = 1 - \frac{1}{n}. \quad (9.36)$$

We see that the correlation function at small delays is suppressed rather than enhanced – see the dashed line in Fig. 3. This *photon antibunching* effect has a very simple explanation: a single photon emitted by the wave source may be absorbed by just one of the detectors. For the initial state $n = 1$, this is the only option, and it is very natural that Eq. (36) predicts no simultaneous counts at $\tau = 0$. Despite this theoretical simplicity, reliable observations of the antibunching have not been carried out until 1977,¹⁹ due to the experimental difficulty of creating Fock states of electromagnetic field oscillators – see Sec. 4 below.

(ii) The Glauber state α . A similar procedure, but now using Eq. (5.155) and its Hermitian conjugate, $\langle \alpha | \hat{a}^\dagger = \langle \alpha | \alpha^*$, yields

Glauber
field
statistics

$$g^{(2)}(0) = \frac{\langle \alpha | \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} | \alpha \rangle}{\langle \alpha | \hat{a}^\dagger \hat{a} | \alpha \rangle^2} = \frac{\alpha^* \alpha^* \alpha \alpha}{(\alpha^* \alpha)^2} = 1, \quad (9.37)$$

for any parameter α . We see that the result is very different result from the Fock states, unless in the latter case $n \rightarrow \infty$. (We know that the Fock and Glauber properties should also coincide for the ground state, but at that state the correlation function's value is uncertain, because there are no photon counts at all.)

(iii) Classical mixture. From Chapter 7, we know that such ensembles cannot be described by single state vectors, and require the density matrix w for their description. In particular, we can use the key Eq. (7.5) to write

$$g^{(2)}(0) = \frac{\text{Tr}(\hat{w} \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a})}{[\text{Tr}(\hat{w} \hat{a}^\dagger \hat{a})]^2}. \quad (9.38)$$

The calculation is easy for an ensemble in thermodynamic equilibrium, because here the density matrix is diagonal in the basis of Fock states n - see Eqs. (7.23)-(7.25):

¹⁹ H. J. Kimble *et al.*, *Phys. Rev. Lett.* **39**, 691 (1977). For a detailed review of phonon antibunching, see, e.g., H. Paul, *Rev. Mod. Phys.* **54**, 1061 (1982).

$$w_{nn'} = W_n \delta_{nn'}, \quad W_n = \frac{1}{Z} \exp\left\{-\frac{E_n}{k_B T}\right\} = \frac{\lambda^n}{\sum_{n=0}^{\infty} \lambda^n}, \quad \text{where } \lambda \equiv \exp\left\{-\frac{\hbar\omega}{k_B T}\right\}. \quad (9.39)$$

So, for the operators in the nominator and denominator of Eq. (38) we also need just the diagonal terms of the operator products that have already been calculated – see Eq. (36). As a result, we get

$$g^{(2)}(0) = \frac{\sum_{n=0}^{\infty} W_n n(n-1)}{\left(\sum_{n=0}^{\infty} W_n n\right)^2} = \frac{\sum_{n=0}^{\infty} \lambda^n n(n-1) \times \sum_{n=0}^{\infty} \lambda^n}{\left(\sum_{n=0}^{\infty} \lambda^n n\right)^2}. \quad (9.40)$$

One of these sums is just the geometric progression,

$$\sum_{n=0}^{\infty} \lambda^n = \frac{1}{1-\lambda}, \quad (9.41)$$

and the remaining two sums may be readily calculated by its differentiation over parameter λ :

$$\begin{aligned} \sum_{n=0}^{\infty} \lambda^n n &= \lambda \sum_{n=0}^{\infty} \lambda^{n-1} n = \lambda \frac{d}{d\lambda} \sum_{n=0}^{\infty} \lambda^n = \lambda \frac{d}{d\lambda} \frac{1}{1-\lambda} = \frac{\lambda}{(1-\lambda)^2}, \\ \sum_{n=0}^{\infty} \lambda^n n(n-1) &= \lambda^2 \sum_{n=0}^{\infty} \lambda^{n-2} n(n-1) = \lambda^2 \frac{d^2}{d\lambda^2} \left(\sum_{n=0}^{\infty} \lambda^n \right) = \lambda^2 \frac{d^2}{d\lambda^2} \frac{1}{1-\lambda} = \frac{2\lambda^2}{(1-\lambda)^3}, \end{aligned} \quad (9.42)$$

and for the correlation function we get an extremely simple result independent of parameter λ and hence of temperature:

$$g^{(2)}(0) = \frac{[2\lambda^2/(1-\lambda)^3][1/(1-\lambda)]}{[\lambda/(1-\lambda)^2]^2} = 2. \quad (9.43) \quad \text{Photon bunching}$$

This is the exactly the photon bunching effect first observed by Hanbury Brown and Twiss (Fig. 3). We see that in contrast to antibunching, this is an essentially classical (statistical) effect. Indeed, Eq. (43) allows a purely classical proof. In the classical theory, the counting rate is proportional to the wave intensity I , so that Eq. (31) is reduced to

$$g^{(2)}(0) = \frac{\langle I^2 \rangle}{\langle I \rangle^2}, \quad \text{with } I \propto \overline{E^2(t)} \propto E_\omega E_\omega^*. \quad (9.44)$$

For a sinusoidal field, the intensity is constant, and $g^{(2)}(0) = 1$. (This is also evident from Eq. (37), because the classical state may be considered as the Glauber state with $\alpha \rightarrow \infty$.) On the other hand, if intensity fluctuates (either in time, or from one experiment to another), the averages should be calculated as

$$\langle I^N \rangle = \int_0^\infty w(I) I^N dI, \quad \text{with } \int_0^\infty w(I) dI = 1, \quad (9.45)$$

where $w(I)$ is the probability density. For the classical (Boltzmann) statistics, the probability is an exponential function of the electromagnetic field energy, and hence its intensity:

$$w(I) = Ce^{-\beta I}, \quad \text{where } \beta \propto 1/k_B T, \quad (9.46)$$

so that Eqs. (48) yield:

$$\begin{aligned} \int_0^\infty C \exp\{-\beta I\} dI &= 1, \quad \text{so that } C = \beta, \\ \langle I^N \rangle &= \int_0^\infty w(I) I^N dI = C \int_0^\infty \exp\{-\beta I\} I^N dI = \frac{1}{\beta^N} \int_0^\infty \exp\{-\xi\} \xi^N d\xi = \begin{cases} 1/\beta, & \text{for } N=1, \\ 2/\beta^2, & \text{for } N=2. \end{cases} \end{aligned} \quad (9.47)$$

Plugging these results into Eq. (44), we get $g^{(2)}(0) = 2$, in a complete agreement with Eq. (43).²⁰

9.3. Spontaneous and stimulated emission

In our simple model for photon counting, considered in the last section, trigger atoms of the photon counter *absorbed* light. Now let us have a look at the opposite process of *spontaneous emission* of photons by an atom in an excited state, still using the same electric-dipole approximation for the atom-to-field interaction. We may still use the Golden Rule for the model depicted in Fig. 6.14, but now the roles have changed: we have to associate operator $\hat{A}$ with the electric dipole moment of the atom, while operator $\hat{B}$ with the electric field, and the continuous spectrum of system b represents the plurality of the electromagnetic field modes into which the spontaneous radiation may happen. Since now the transition *increases* the energy of the electromagnetic field, after the multiplication of the field bra-ket by $\exp\{i\omega t\}$, we may keep only the photon *creation* operator whose time evolution compensates this fast “rotation”. As a result, the Golden Rule takes the following form:

Spontaneous
photon
emission
rate

$$\Gamma_s = \pi\omega \left| \langle fin | \hat{a}^\dagger | 0 \rangle \right|^2 \left| \langle fin | \hat{\mathbf{d}} \cdot \mathbf{e}(\mathbf{r}) | ini \rangle \right|^2 \rho_{fin}, \quad (9.48)$$

where all operators and states are time-independent, and ρ_{fin} is now the density of finite states of the electromagnetic field – which in this problem plays the role of atom’s environment. Here the electromagnetic field has been assumed to be initially in the ground state – the assumption that will be altered later in this section.

Relation (48), together with Eq. (19), shows that in order for field’s matrix element be different from zero, the finite state of the field has to be the first excited Fock state, $n = 1$. (By the way, *this* is exactly the most practicable way of generating an excited Fock state of a field oscillator field – whose existence was taken for granted in our discussion in Sec. 2.) With that, Eq. (48) yields

$$\Gamma_s = \pi\omega \left| \langle fin | \hat{\mathbf{d}} \cdot \mathbf{e}(\mathbf{r}) | ini \rangle \right|^2 \rho_{fin} = \pi\omega \left| \langle fin | \hat{d}_e(\mathbf{r}) | ini \rangle \right|^2 \rho_{fin}, \quad (9.49)$$

²⁰ For some field states, including the squeezed ground states ξ discussed in the end of Sec. 5.5, values $g^{(2)}(0)$ may be even higher than 2 – the so-called *super-bunching*. Analysis of one particular case of super-bunching is offered to the reader – see the exercise problem list.

where the density ρ_{fin} of excited electromagnetic field states should be calculated at energy $\hbar\omega$, and e_d is the component of the vector $\mathbf{e}(\mathbf{r})$ along the electric dipole direction.²¹ For plane waves, the calculation of this density was our first step in this course – see Eq. (1.1).²² From it, we get

$$\rho_{\text{fin}} \equiv \frac{dN}{dE} = V \frac{8\pi\nu^2}{c^3} \frac{d\nu}{dE} = V \frac{\omega^2}{\pi^2 \hbar c^3}, \quad (9.50)$$

where the bounding volume V should be large enough to ensure spectrum's virtual continuity. Because of that, in the normalization condition used to simplify Eq. (9), we may consider $e^2(\mathbf{r})$ constant. Let us present the square of this vector as a sum of squares of its three perpendicular components (one of those, e_d , aligned with the dipole direction), due to space isotropy we may write

$$e^2 \equiv e_d^2 + e_{\perp 1}^2 + e_{\perp 2}^2 = 3e_d^2. \quad (9.51)$$

As a result, the normalization condition yields

$$e_d^2 = \frac{1}{3\varepsilon_0 V}. \quad (9.52)$$

and Eq. (49) gives the famous (and very important) formula²³

$$\Gamma_s = \frac{1}{4\pi\varepsilon_0} \frac{4\omega^3}{3\hbar c^3} |\langle fin | \hat{\mathbf{d}} | ini \rangle|^2 = \frac{1}{4\pi\varepsilon_0} \frac{4\omega^3}{3\hbar c^3} \langle fin | \hat{\mathbf{d}} | ini \rangle \cdot \langle ini | \hat{\mathbf{d}} | fin \rangle^*. \quad (9.53)$$

Free-space
spontaneous
emission
rate

Leaving a comparison of this formula with the classical theory of radiation,²⁴ and the exact evaluation of Γ_s for a particular transition in the hydrogen atom, for reader's exercises, let me just estimate its order of magnitude. Assuming that $d \sim er_B \equiv e\hbar^2/m_e(e^2/4\pi\varepsilon_0)$ and $\hbar\omega \sim E_H \equiv m_e(e^2/4\pi\varepsilon_0)^2/\hbar^2$, and taking into account the definition (6.62) of the fine structure constant $\alpha \approx 1/137$, we get

$$\frac{\Gamma}{\omega} \sim \left(\frac{e^2}{4\pi\varepsilon_0 \hbar c} \right)^3 \equiv \alpha^3 \sim 3 \times 10^{-7}. \quad (9.54)$$

This estimate says that the emission lines at atomic transitions are typically very sharp. With the present-day availability of high-speed electronics, it also makes sense to evaluate the time scale $\tau = 1/\Gamma$ of the typical quantum transition: for a typical optical frequency $\omega \sim 3 \times 10^{15} \text{ s}^{-1}$, it is close to 1 ns. This is

²¹ Here I have smuggled back the sum over all electromagnetic field modes j – see Eq. (16). Since in the quasistationary approximation, $k_j a \ll 1$, which is necessary for the interaction presentation by Eq. (24), matrix elements (49) are independent on k_j , the summation is reduced to the calculation of the total ρ_{fin} for all modes.

²² Note the essential dependence of Eq. (50), and hence of Eq. (53) on the field geometry; all following formulas of this section are valid for free 3D space only. If the same atom is placed into a high- Q resonant cavity (see, e.g., EM 7.9), the rate of its photon emission is strongly suppressed at frequencies between the cavity resonances (where $\rho_{\text{fin}} \rightarrow 0$) – see, e.g., the review of first experiments by S. Haroche and D. Klepner, *Phys. Today* **42**, 24 (Jan. 1989). On the other hand, the emission is strongly (by a factor $\sim (\lambda^3/V)Q$, where V is cavity's volume) enhanced at resonance frequencies – the so-called *Purcell effect*, discovered by E. Purcell already in the 1940s. For a brief discussion of these and other quantum effects in cavities, see the next section.

²³ An equivalent expression was first obtained in 1930 by V. Weisskopf and E. Wigner, so that the whole calculation is sometimes referred to as the *Weisskopf-Wigner theory*.

²⁴ See, e.g., EM Sec. 8.2, in particular Eq. (8.28).

exactly the time constant that determines the photon counting statistics of the emitted radiation – see Fig. 3. Colloquially, this is the temporal scale of the photon spontaneously emitted by an atom.²⁵

Note, however, that the above estimate of τ is only valid for a transition with a non-vanishing dipole matrix element. If it equals zero – say, due to the initial and final state symmetry – the dipole transitions are “forbidden”. (Another commonly used term is the *transition selection rules*.²⁶) The “forbidden” transition may still take place due to a different, smaller interaction (say, via a magnetic dipole field of the atom, or its quadrupole electric field²⁷), but would take much longer. In some cases the increase of τ is rather dramatic – sometimes to hours! Such long-lasting radiation is called *luminescence* – or *fluorescence* if the initial atom’s excitation was due to an external radiation of higher frequency, followed first by non-radiative transitions down the energy level ladder.

Now let us consider a more general case when the electromagnetic field is initially in an arbitrary Fock state n , and from it may either get energy from the atomic system (*photon emission*) or, vice versa, give it back to the atom (*photon absorption*). For the photon emission rate, an evident generalization of Eq. (48) gives

$$\frac{\Gamma_e}{\Gamma_s} \equiv \frac{\Gamma_{n \rightarrow fin}}{\Gamma_{0 \rightarrow 1}} = \frac{\left| \langle fin | \hat{a}^\dagger | n \rangle \right|^2}{\left| \langle 1 | \hat{a}^\dagger | 0 \rangle \right|^2}, \quad (9.55)$$

where both bra-kets may be taken in the Schrödinger picture, and Γ_s is the spontaneous emission rate (53) of the same atomic system. This relation, with the account of Eq. (19), shows that at photon emission, the final field state fin has to be the Fock state with $n' = n + 1$, and that

Total
(stimulated +
spontaneous)
emission rate

$$\Gamma_e = (n + 1) \Gamma_s. \quad (9.56)$$

Thus the initial field increases the photon emission rate; this effect is called the *stimulated emission of radiation*. Note that the spontaneous emission may be considered as a particular case of stimulated emission for $n = 0$, and interpreted as the emission stimulated by zero-point fluctuations of the electromagnetic field.

On the other hand, in accordance with the arguments of Sec. 2, for the description of radiation *absorption* the photon creation operator has to be replaced with the annihilation one, to get

$$\frac{\Gamma_a}{\Gamma_s} = \frac{\left| \langle fin | \hat{a} | n \rangle \right|^2}{\left| \langle 1 | \hat{a}^\dagger | 0 \rangle \right|^2}. \quad (9.57)$$

²⁵ The scale $c\tau$ of the spatial extension of the corresponding wave packet is surprisingly macroscopic – in the range of a few millimeters. Such “human” size of the emitted photons makes the optical table the key component of many optical experiments.

²⁶ As was already mentioned in Sec. 5.6, for a single particle moving in a spherically-symmetric potential (e.g., a hydrogen-like atom), the selection rules are simple: the only allowed electric-dipole transitions are those with $\Delta l \equiv l_{fin} - l_{ini} = \pm 1$ and $\Delta m \equiv m_{fin} - m_{ini} = 0$. The simplest example of the transition that does *not* satisfy this rule is that between states with $n = 2$ and $n = 1$, both with $l = 0$; because of that, the lifetime of the lowest excited s -state in hydrogen is as long as ~ 0.15 s.

²⁷ See, e.g., EM Sec. 8.9.

According to this equation, the final state of the field at absorption is the Fock state with $n' = n - 1$, and Eq. (57) yields²⁸

$$\Gamma_a = n\Gamma_s. \quad (9.58)$$

Photon
absorption
rate

Results (56) and (58) are usually be formulated in terms of between the *Einstein coefficients* A and B defined in the way shown in Fig. 4, where the two energy levels are those of the atom, Γ_a is the rate of energy absorption from the electromagnetic field, and Γ_e is that of the energy emission into the field. In this notation, Eqs. (56) and (58) say

$$A_{21} = B_{21} = B_{12}, \quad (9.59)$$

Einstein
coefficients'
relation

because each of these coefficients equals the spontaneous emission rate Γ_s .

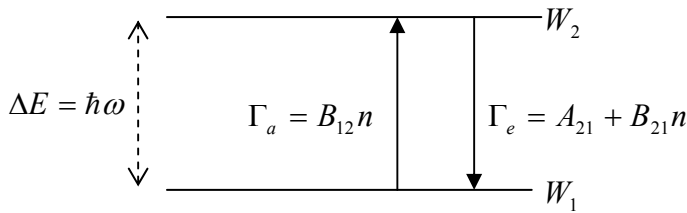


Fig. 9.4. The Einstein coefficients on the atomic energy spectrum diagram.

It is curious that from this point, there is just one step to an alternative derivation of the Bose-Einstein statistics for photons. Indeed, in the thermodynamic equilibrium, the average probability flows between levels 1 and 2 should be equal:

$$W_2 \langle \Gamma_e \rangle = W_1 \langle \Gamma_a \rangle, \quad (9.60)$$

where W_1 and W_2 are the probabilities for the atomic system to be on the corresponding levels, so that Eqs. (56) and (58) yield

$$W_2 \Gamma_s \langle 1 + n \rangle = W_1 \Gamma_s \langle n \rangle, \quad \text{i.e.} \quad \frac{W_2}{W_1} = \frac{\langle n \rangle}{\langle n \rangle + 1}. \quad (9.61)$$

But, on the other hand, for the atomic subsystem, only weakly coupled to its electromagnetic environment, we ought to have the Gibbs distribution of probabilities:

$$\frac{W_2}{W_1} = \frac{\exp\{-E_2 / k_B T\}}{\exp\{-E_1 / k_B T\}} = \exp\left\{-\frac{\Delta E}{k_B T}\right\} = \exp\left\{-\frac{\hbar\omega}{k_B T}\right\}. \quad (9.62)$$

Requiring Eqs. (61) and (62) to give the same result for the probability ratio, we get the Bose-Einstein distribution for the electromagnetic field in equilibrium:

$$\langle n \rangle = \frac{1}{\exp\{\hbar\omega / k_B T\} - 1}, \quad (9.63)$$

the same as obtained in Sec. 7.1 by other means – see Eqs. (7.26).

²⁸ Relations (56) and (58) were conjectured, from very general arguments, by A. Einstein as early as in 1916.

Another, very important implication of Eqs. (56) and (58) is the possibility to achieve the stimulated emission coherence by level *occupancy* (or “population”) *inversion*. Indeed, if $W_2 > W_1$, then the net power flow from the atomic system into the electromagnetic field,

$$\text{power} = \hbar\omega \times \Gamma_s [W_2(\langle n \rangle + 1) - W_1\langle n \rangle], \quad (9.64)$$

may be positive. The necessary inversion may be produced using several ways, notably by a intensive quantum transitions to level 2 from an even higher level (which, in turn, is populated, e.g., by absorption of an external radiation, called *pumping*, at a higher frequency.)

A less obvious feature of the stimulated emission is spelled out by Eq. (55): again, it shows that the final state of the field after the absorption of energy $\hbar\omega$ from the atom is a pure (coherent) Fock state $(n + 1)$. Colloquially, one may say that the new, $(n + 1)^{\text{st}}$ photon emitted from the atom is automatically in phase with the n photons that had been in the field mode initially.²⁹ The idea of stimulated emission of coherent radiation using population inversion³⁰ was implemented in the early 1950s in the microwave range (*masers*) and in 1960 in the optical range (*lasers*). Nowadays, lasers are ubiquitous and constitute one of cornerstones of our technological civilization.

A quantitative discussion of laser operation is beyond the framework of this course, and I have to refer the reader to special literature,³¹ and would only like to mention only two key points:

(i) In a typical laser, each generated electromagnetic field mode is in the Glauber (rather than the Fock) state, so that Eqs. (56) and (58) are applicable only for n is averaged over the Fock-state decomposition of the Glauber state – see Eq. (5.165).

(ii) Since in a typical laser $\langle n \rangle \gg 1$, its operation may be well described using quasi-classical theories that use Eq. (64) to describe the electromagnetic energy balance (with the addition of a term describing the energy loss due to field absorption in external components of the laser, including the useful load), plus the equation describing the balance of occupancies $W_{1,2}$ due to all inter-level transitions – similar to Eq. (60), but including also the contribution(s) from the particular population inversion mechanism used in the laser. At this approach, the role of quantum mechanics is essentially reduced to the calculation of parameter Γ_s .

The role becomes more prominent if one needs to describe *fluctuations* of the laser field. Here two approaches are possible, following the two options discussed in Chapter 7. If the fluctuations are relatively small, one can linearize the Heisenberg equations of motion of the field oscillator operators near their stationary-lasing “values”, with the Langevin “forces” (also time-dependent operators) to describe the fluctuation sources, and use these Heisenberg-Langevin equations to the radiation fluctuations, just as was described in Sec. 7.5. On the other hand, near the lasing threshold the field fluctuations are relatively strong, smearing the phase transition between the no-lasing and lasing states. Here the linearization is not an option, but one can use the density-matrix approach described in Sec. 7.6, for the fluctuation analysis.³²

²⁹ It is straightforward to show that this fact is also true if the field is initially in the Glauber state – which is more typical for lasers.

³⁰ This idea has been traced back at least to an obscure 1939 publication by V. Fabrikant.

³¹ I can recommend, for example, P. W. Milloni and J. H. Eberly, *Laser Physics*, 2nd ed., Wiley, 2010, and a less technical text by A. Yariv, *Quantum Electronics*, 3rd ed., Wiley, 1989.

³² This path has been developed (also in the mid-1960s), by several researchers, notably including M. Sully and W. Lamb – see, e.g., M. Sargent III, M. Scully, and W. Lamb, Jr., *Laser Physics*, Westview, 1977. Note that

9.4. Cavity QED

Now I have to mention, at least in passing, the *cavity quantum electrodynamics* (usually called *cavity QED* for short) – an art and science of creating and using entanglement between quantum states of a single atomic system (either an atom, or an ion, or a molecule, etc.) and the electromagnetic field in a macroscopic volume called the *resonant cavity* (or just “resonator”, or just “cavity”). This field is very popular nowadays, especially in the context of the quantum computation and communication research discussed in Sec. 8.5.³³

Let me start its discussion by noting that the narrative of two last sections was based on an implicit assumption that the energy spectrum of the electromagnetic field interacting with an atomic system is essentially continuous. This assumption has justified the use of Golden Rule, implying that the emitted radiation is spread among many field modes, effectively losing their coherence with the initial quantum state of the atom. However, this assumption becomes invalid if the electromagnetic field is contained inside a relatively small volume, with a linear size comparable with the radiation wavelength. Classical electrodynamics shows³⁴ that if the walls of such a cavity mostly reflect, rather than absorb, radiation, so that in the crude approximation the power dissipation may be disregarded, then particular solutions $\mathbf{e}_j(\mathbf{r})$ of the Helmholtz equation (5) correspond to discrete, well separated mode wavenumbers k_j and hence well separated eigenfrequencies ω_j . Due to the energy conservation, an atomic transition corresponding to energy $\Delta E = |E_{\text{ini}} - E_{\text{fin}}|$ may be effective only if the corresponding quantum oscillation frequency $\Omega \equiv \Delta E/\hbar$ is close to one of ω_j and hence relatively far from other eigenfrequencies.³⁵ As a result, the quantum states of a single atomic system and the resonant electromagnetic mode may become entangled.

A very popular approximation for the qualitative description of this effect is the so-called *Rabi model*,³⁶ in which the atom is treated as a two-level system³⁷ interacting with a single electromagnetic field mode of the resonant cavity. As the reader knows well from Chapters 4-6, any two-level (“spin-1/2”) system may be described by Hamiltonian $\mathbf{c} \cdot \hat{\boldsymbol{\sigma}}$, and we may always select the state basis in that the Hamiltonian is diagonal:

$$\hat{H}_{\text{atom}} = c\hat{\sigma}_z \equiv \frac{\hbar\Omega}{2}\hat{\sigma}_z, \quad (9.65)$$

where $\hbar\Omega \equiv 2c$ is the energy difference between the eigenenergies in the absence of interaction with the field. Next, according to Eq. (17), ignoring the constant ground-state energy $\hbar\omega/2$ (that may be added to

while the laser radiation fluctuations may look like a peripheral issue, pioneering research in that field has led to the development of the general theory of open quantum systems (which was discussed in Chapter 7), that has much broader applications.

³³ This popularity was demonstrated, for example, by the 2012 Nobel Prize in Physics award to cavity QED experimentalists S. Haroche and D. Wineland.

³⁴ See, e.g., EM Sec. 7.9.

³⁵ On the contrary, if Ω is far from any ω_j , the interaction is much suppressed; in particular, the spontaneous emission rate may be much lower than that given by Eq. (53) – so that this result is not as fundamental as it may look.

³⁶ After the pioneering work by I. Rabi in 1936-37.

³⁷ As was shown in Sec. 6.5, this model is justified, e.g., if transitions between all other energy level pairs have considerably different frequencies.

the final energy in the very end – if necessary), the contribution of a single mode of eigenfrequency ω to the Hamiltonian is

$$\hat{H}_{\text{cavity}} = \hbar\omega\hat{a}^\dagger\hat{a}. \quad (9.66)$$

Finally, according to Eq. (16a), in quantum electrodynamics the electric field of the mode may be presented as

$$\hat{\mathcal{E}}(\mathbf{r}, t) = \frac{1}{i} \left(\frac{\hbar\omega}{2} \right)^{1/2} \mathbf{e}(\mathbf{r}) \left(\hat{a} - \hat{a}^\dagger \right), \quad (9.67)$$

so that in the electric-dipole approximation (24), the cavity-atom interaction may be presented as a product of the field by one of Cartesian components (say, σ_y) of the “spin” operator:³⁸

$$\hat{H}_{\text{int}} = \text{const} \times \hat{\sigma}_y \times \mathcal{E} = \text{const} \times \hat{\sigma}_y \times \left(\frac{\hbar\omega}{2} \right)^{1/2} \frac{1}{i} \left(\hat{a} - \hat{a}^\dagger \right) = i\hbar\kappa\hat{\sigma}_y \left(\hat{a} - \hat{a}^\dagger \right), \quad (9.68)$$

where κ is a coupling constant (with the dimension of frequency). The sum of these terms is called the *Rabi Hamiltonian*,

Rabi
Hamiltonian

$$\hat{H} \equiv \hat{H}_{\text{atom}} + \hat{H}_{\text{cavity}} + \hat{H}_{\text{int}} = \frac{\hbar\Omega}{2} \hat{\sigma}_z + \hbar\omega\hat{a}^\dagger\hat{a} + i\hbar\kappa\hat{\sigma}_y \left(\hat{a} - \hat{a}^\dagger \right). \quad (9.69)$$

Despite its apparent simplicity, using this Hamiltonian for calculations is not that simple. For example, an exact quasi-analytical expression for its eigenenergies (as zeros of a Taylor series in parameter κ , with coefficients determined by a recurrence relation) was found only recently.³⁹ Only in the case when the electromagnetic field is very intensive and hence may be treated as the classical one, the results following from Eq. (69) are reduced to the Rabi oscillations discussed in Sec. 6.3.

In the opposite case when the field oscillator is in an essentially quantum state, $\langle \hat{a}^\dagger\hat{a} \rangle \sim 1$, Eq. (69) may be simplified in a different way, assuming that frequencies Ω and ω are very close, and the atom-to-cavity interaction is relatively weak, so that magnitudes of the coupling constant κ and the *detuning* parameter (similar to parameter Δ used in Sec. 6.5),

$$\xi \equiv \Omega - \omega, \quad (9.70)$$

are both much smaller than $\Omega \approx \omega$. To discuss this limit, it is convenient to use the *spin ladder operators* defined absolutely similarly for those of the orbital angular momentum – see Eqs. (5.182):

$$\hat{\sigma}_\pm \equiv \hat{\sigma}_x \pm i\hat{\sigma}_y, \text{ so that } \hat{\sigma}_y = \frac{\hat{\sigma}_+ - \hat{\sigma}_-}{2i}. \quad (9.71)$$

From Eq. (4.105), it is easy to find matrices of these operators (in the standard z -basis),

$$\sigma_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}, \quad (9.72)$$

³⁸ The exact choice of this component is not important, while the formulas simplify if it is proportional to either pure σ_x or pure σ_y .

³⁹ D. Braak, *Phys. Rev. Lett.* **107**, 100401 (2011).

and their commutation rules – that are naturally similar to Eqs. (5.183):

$$[\hat{\sigma}_+, \hat{\sigma}_-] = 4\hat{\sigma}_z, \quad [\hat{\sigma}_z, \hat{\sigma}_\pm] = \pm 2\hat{\sigma}_\pm. \quad (9.73)$$

In this notation, the Rabi Hamiltonian looks like

$$\hat{H} = \frac{\hbar\Omega}{2} \hat{\sigma}_z + \hbar\omega \hat{a}^\dagger \hat{a} + \frac{\hbar\kappa}{2} (\hat{\sigma}_+ - \hat{\sigma}_-) (\hat{a} - \hat{a}^\dagger), \quad (9.74)$$

and it is straightforward to use Eq. (4.199) and (73) to derive the Heisenberg-picture equations of motion for the involved operators. (Doing this, we have to remember that operators of the “spin” subsystem, on one hand, and of the field mode, on the other hand, are defined in different Hilbert spaces and hence commute – at least at coinciding time moments.) The result (so far, exact!) is

$$\begin{aligned} \dot{\hat{a}} &= -i\omega \hat{a} - \frac{i\kappa}{2} (\hat{\sigma}_+ - \hat{\sigma}_-), & \dot{\hat{a}}^\dagger &= i\omega \hat{a}^\dagger + \frac{i\kappa}{2} (\hat{\sigma}_+ - \hat{\sigma}_-), \\ \dot{\hat{\sigma}}_\pm &= \pm i\Omega \hat{\sigma}_\pm + i2\kappa (\hat{a} - \hat{a}^\dagger) \hat{\sigma}_z, & \dot{\hat{\sigma}}_z &= i\kappa (\hat{a}^\dagger - \hat{a}) (\hat{\sigma}_+ + \hat{\sigma}_-). \end{aligned} \quad (9.75)$$

Now note that at negligible coupling, $\kappa \rightarrow 0$, equations (75) have very simple solutions,

$$\hat{a}(t) \propto e^{-i\omega t}, \quad \hat{a}^\dagger(t) \propto e^{i\omega t}, \quad \hat{\sigma}_\pm(t) \propto e^{\pm i\Omega t}, \quad \hat{\sigma}_z(t) \approx \text{const}, \quad (9.76)$$

and small terms proportional to κ in the right-hand parts of Eqs. (75) cannot affect these time evolution laws dramatically even if κ is not exactly zero (but small). Of those terms, ones with frequencies close to the “basic” frequency of each variable would act in resonance and hence may have a substantial impact on system dynamics, while non-resonant terms may be ignored. In this rotating-wave approximation (RWA), used several times before in this course, Eqs. (*) are reduced to a much simpler system of equations:

$$\begin{aligned} \dot{\hat{a}} &= -i\omega \hat{a} - \frac{i\kappa}{2} \hat{\sigma}_-, & \dot{\hat{a}}^\dagger &= i\omega \hat{a}^\dagger + \frac{i\kappa}{2} \hat{\sigma}_+, \\ \dot{\hat{\sigma}}_+ &= i\Omega \hat{\sigma}_+ + i2\kappa \hat{a}^\dagger \hat{\sigma}_z, & \dot{\hat{\sigma}}_- &= -i\Omega \hat{\sigma}_- - i2\kappa \hat{a} \hat{\sigma}_z, & \dot{\hat{\sigma}}_z &= i\kappa (\hat{a}^\dagger \hat{\sigma}_- - \hat{a} \hat{\sigma}_+). \end{aligned} \quad (9.77)$$

Alternatively, these equations of motion may be obtained from the Rabi Hamiltonian after it has been cleared of the terms proportional to $\hat{\sigma}_+ \hat{a}^\dagger$ and $\hat{\sigma}_- \hat{a}$, that oscillate fast and hence self-average to virtually zero:

$$\hat{H} = \frac{\hbar\Omega}{2} \hat{\sigma}_z + \hbar\omega \hat{a}^\dagger \hat{a} + \frac{\hbar\kappa}{2} (\hat{\sigma}_+ \hat{a} + \hat{\sigma}_- \hat{a}^\dagger), \quad \text{at } \kappa, |\xi| \ll \omega, \Omega. \quad (9.78)$$

Janes-Cummings
Hamiltonian

This is the famous *Janes-Cummings Hamiltonian*,⁴⁰ which is central to the cavity QED and its applications.⁴¹ In order to find its eigenstates and eigenenergies, let us note that at negligible interaction

⁴⁰ It was first proposed and analyzed in 1963 by two electronic engineers, E. Janes and F. Cummings, and it took the physics community a while to recognize and acknowledge the fundamental importance of that work.

⁴¹ In most applications, Hamiltonian (78) is augmented by additional term(s) describing, for example, incoming radiation and/or coupling to environment, say due to the electromagnetic energy loss in the cavity walls – see Eq. (7.68).

($\kappa \rightarrow 0$), the spectrum of the total energy E of the system, that in this limit is the sum of two independent contributions from the atomic (“spin”) and resonant-cavity subsystems,

$$E|_{\kappa=0} = \pm \frac{\hbar\Omega}{2} + \hbar\omega n \equiv E_n \pm \frac{\hbar\xi}{2}, \quad (9.79)$$

consists⁴² of close level pairs (Fig. 5) centered to values

$$E_n \equiv \hbar\omega \left(n - \frac{1}{2} \right), \quad \text{with } n = 1, 2, \dots \quad (9.80)$$

(At the exact resonance $\omega = \Omega$, i.e. at $\xi = 0$, each pair merges into one double-degenerate level E_n .)

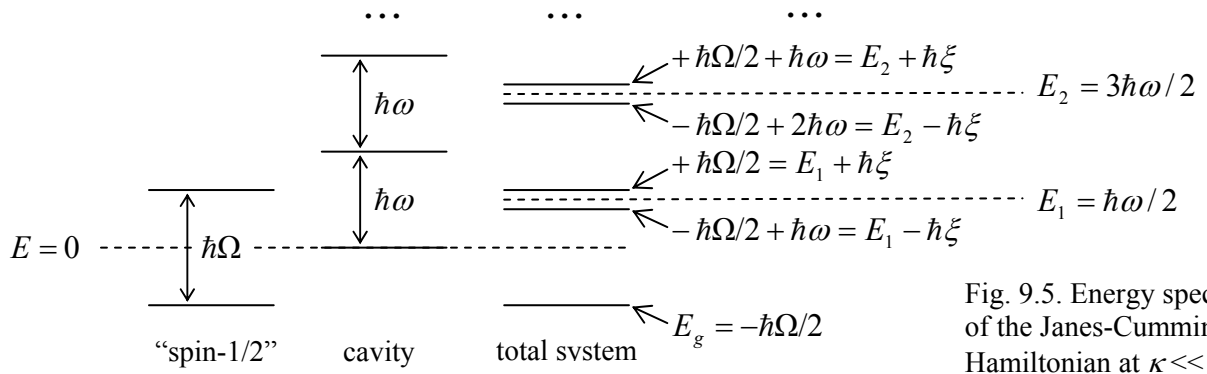


Fig. 9.5. Energy spectrum of the Janes-Cummings Hamiltonian at $\kappa \ll |\xi|$.

Since at $\kappa \rightarrow 0$ the two subsystems do not interact, the eigenstates corresponding to the sublevels of n -th pair may be represented by products of their independent ket-vectors:

$$|+\rangle \equiv |\uparrow\rangle \otimes |n-1\rangle \quad \text{and} \quad |-\rangle \equiv |\downarrow\rangle \otimes |n\rangle. \quad (9.81)$$

As we know from Chapter 6, weak interaction leads to strong hybridization of quantum states with close energies (in this case, two states (81) with each pair with the same n) and their negligible mixing with other states. Hence, at $0 < \kappa \ll \omega \approx \Omega$, a good approximation of an eigenstate with $E \approx E_n$ is given by a linear superposition of states (81):

$$|\alpha\rangle = c_+ |\uparrow\rangle \otimes |n-1\rangle + c_- |\downarrow\rangle \otimes |n\rangle, \quad (9.82)$$

with certain c -number coefficients $c_{\pm}$. This relation describes the entanglement of atomic eigenstates $\uparrow$ and $\downarrow$ with Fock states n and $n-1$ of the field mode.

Let me leave the (straightforward) calculation of coefficients $c_{\pm}$ and eigenenergies of the two entangled state pairs for reader's exercise. This calculation shows, in particular, that at the exact resonance ($\omega = \Omega$), $|c_+| = |c_-| = 1/\sqrt{2}$ for both states of each pair. This fact may be interpreted as a (coherent!) equal sharing of an energy quantum $\hbar\omega = \hbar\Omega$ by the atom and the cavity.

A by-product of the calculation of $c_{\pm}$ is the fact that the dynamics of state α described by Eq. (82) is similar to that of the generic two-level system that was repeatedly discussed in this course - first

⁴² Besides the non-degenerate ground state level $E_g = -\hbar\Omega/2$.

time in Sec. 2.6 and then in Chapters 4-6. In particular, if the composite system had been initially prepared to be in one component state, for example $|\uparrow\rangle\otimes|0\rangle$ (i.e. the atom excited, while the cavity in its ground state) and allowed to evolve on its own, after some time interval it may be found in the counterpart state $|\downarrow\rangle\otimes|1\rangle$, including the first excited Fock state $n = 1$ of the field mode. This is one more (resonant) version of the same method for generation of Fock states of electromagnetic field which was discussed in Sec. 3.⁴³

Unfortunately, my time devoted to cavity QED is over, and for further reading I have to refer the reader to special literature.⁴⁴

9.5. The Klein-Gordon and relativistic Schrödinger equations

Now let us discuss the basics of relativistic quantum mechanics of particles with a nonvanishing rest mass m - i.e., in terms of Eq. (1), the intermediate range of energies: $E \sim mc^2$, i.e. for $p \sim mc$. Historically, the first attempt⁴⁵ to extend the nonrelativistic wave mechanics into the relativistic energy range was based on performing the same transitions from classical observables to their quantum-mechanical operators as in the nonrelativistic limit:

$$\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla, \quad E \rightarrow \hat{H} = i\hbar \frac{\partial}{\partial t}. \quad (9.83)$$

Substitution of these operators, acting on the Schrödinger-picture wavefunction $\Psi(\mathbf{r}, t)$, into the classical relation between the energy E and momentum $\mathbf{p}$ (for of a free particle) leads to the following equations:

Table 9.1. Deriving the Klein-Gordon equation for a free relativistic particle.⁴⁶

	Nonrelativistic limit	Relativistic case
Classical mechanics	$E = \frac{1}{2m} p^2$	$E^2 = c^2 p^2 + (mc^2)^2$
Wave mechanics	$i\hbar \frac{\partial}{\partial t} \Psi = \frac{1}{2m} (-i\hbar\nabla)^2 \Psi$	$\left(i\hbar \frac{\partial}{\partial t}\right)^2 \Psi = c^2 (-i\hbar\nabla)^2 \Psi + (mc^2)^2 \Psi$

⁴³ Another important corollary of the level structure shown in Fig. 5 is the Purcell effect already mentioned in Sec. 3. As we already know from Chapter 7, if the system is coupled to environment, the coupling suppresses its quantum coherence, in our case the coherence between components of each pair (82). As a result, if the atom is initially in state $\uparrow$ with higher energy (79), it may perform incoherent (dissipative) transition to the lower-energy state $\downarrow$, giving energy $\hbar\omega$ to the cavity ($n - 1 \rightarrow n$), which rapidly drains it into the environment. Since the total energies of these initial and finite states are close (Fig. 5), the rate of such transitions may be much higher than in free space. The quantitative analysis of such enhancement is left for reader's exercise.

⁴⁴ I can recommend, for example, either C. Gerry and P. Knight, *Introductory Quantum Optics*, Cambridge U. Press, 2005' or G. Agarwal, *Quantum Optics*, Cambridge U. Press, 2012.

⁴⁵ This approach was suggested almost simultaneously in 1926-1927 by (at least) V. Fock, E. Schrödinger, O. Klein and W. Gordon, J. Kudar, T. de Donder and F.-H. van der Dungen, and L. de Broglie.

⁴⁶ Note that in the sense of Eq. (1), in the nonrelativistic column of this table, the energy is referred to the rest energy mc^2 , while in the relativistic column, to zero.

The resulting equation for the nonrelativistic limit is just the usual Schrödinger equation (1.28) for a free particle. Its relativistic generalization, usually rewritten as

Klein-Gordon equation

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \Psi + \mu^2 \Psi = 0, \quad \text{with } \mu \equiv \frac{mc}{\hbar}, \quad (9.84)$$

is called the *Klein-Gordon* (or sometimes “Klein-Gordon-Fock”) *equation*. The most fundamental solutions of this equation are the same plane, monochromatic waves

$$\Psi(\mathbf{r}, t) \propto \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\}. \quad (9.85)$$

as in the nonrelativistic case. Indeed, such waves are eigenstates of operators (83), with eigenvalues

$$\mathbf{p} = \hbar \mathbf{k}, \quad E = \hbar \omega, \quad (9.86)$$

so that their substitution into Eq. (84) immediately returns us to Eq. (1) with replacements (86):

$$E_{\pm} = \hbar \omega_{\pm} = \pm \left[(\hbar c k)^2 + (mc^2)^2 \right]^{1/2}. \quad (9.87)$$

Though one may say that this dispersion relation is just a simple combination of the classical relation (1) and the same basic quantum-mechanical relations (86) as in nonrelativistic limit, it attracts our attention to the fact that energy $\hbar \omega$ as a function of momentum $\hbar \mathbf{k}$ has two rather than one branches, with $E_-(\mathbf{p}) = -E_+(\mathbf{p})$ – see Fig. 6a.

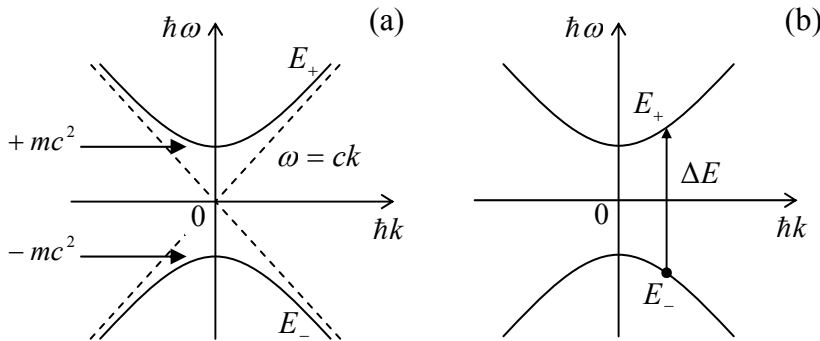


Fig. 9.6. (a) Free-particle dispersion relation resulting from the Klein-Gordon and Dirac equations, and (b) creation of a particle-antiparticle pair from the vacuum.

Historically, this fact has played a very important role for spurring the fundamental idea of *particle-antiparticle pairs*. In this idea (very similar to the concept of electrons and holes in semiconductors, which was discussed in Sec. 2.8), what we call the vacuum actually corresponds to all states of the lower branch, with energies $E_-(\mathbf{p}) < 0$, being filled, while the states on the upper branch, with energies $E_+(\mathbf{p}) > 0$, being empty. Then an externally supplied energy

$$\Delta E = E_+ - E_- = E_+ + (-E_-) \geq 2mc^2 > 0 \quad (9.88)$$

may bring the system from the lower branch to the upper one (Fig. 6b). The resulting excited state is interpreted as a combination of a particle (formally, of the infinite spatial extension) with energy E_+ and momentum $\mathbf{p}$, and a “hole” (antiparticle) of *positive* energy ($-E_-$) and momentum $-\mathbf{p}$. This idea⁴⁷ has led

⁴⁷ Due to the same P. A. M. Dirac!

to a search for, and discovery of the positron: electron's antiparticle with charge $q = +e$, in 1932, and later of the antiproton and other antiparticles.

Free particles of a finite spatial extension may be described, in this approach, just in the nonrelativistic Schrödinger equation, by wave packets: linear superpositions of de-Broglie waves (85) with close wave vectors $\mathbf{k}$, and ω given by Eq. (87), with the positive sign for the “usual” particles, and negative sign for antiparticles – see Fig. 6a above. Note that in order to form, from a particle's wave packet, a similar wave packet for the antiparticle, with the same phase and group velocities (2.33) in each direction, we need to change the sign not only before ω , but also before $\mathbf{k}$, i.e. to replace all component wavefunctions (85), and hence the full wavefunction, with their complex conjugates.

Of more formal properties of the equation, it is easy to prove that its solutions satisfy the same continuity equation (1.52) with the probability current density $\mathbf{j}$ still given by Eq. (1.47), but a different expression for the probability density w - which becomes very similar to that for $\mathbf{j}$:

$$w = \frac{i\hbar}{2mc^2} \left(\Psi^* \frac{\partial \Psi}{\partial t} - \text{c.c.} \right), \quad \mathbf{j} = \frac{i\hbar}{2m} (\Psi \nabla \Psi^* - \text{c.c.}). \quad (9.89)$$

(In the nonrelativistic limit $v/c \rightarrow 0$, Eq. (84) allows a reduction of the first relation to Eq. (1.22): $w \rightarrow \Psi \Psi^*$.)

The Klein-Gordon equation may be readily generalized to describe a single particle moving in external fields; for example, the electromagnetic field effects on a particle with charge q may be described by the same replacement as in the nonrelativistic limit (see Sec. 3.1):⁴⁸

$$\hat{\mathbf{p}} \rightarrow \hat{\mathbf{P}} - q\mathbf{A}(\mathbf{r}, t), \quad \hat{H} \rightarrow \hat{H} - q\phi(\mathbf{r}, t), \quad (9.90)$$

where $\hat{\mathbf{P}} = -i\hbar\nabla$ is the canonical momentum operator (3.25), and the vector- and scalar potentials, $\mathbf{A}$ and ϕ , should be treated appropriately – either as c -number functions if the electromagnetic field quantization is unimportant, or as operators (see Secs. 1-4 above) if it is.

However, the practical value of the relativistic Schrödinger equation is rather limited, because of two main reasons. First of all, it does not give the correct description of particles with spin. For example, for the hydrogen-like atom, i.e. the motion of an electron with electric charge $-e$ in the Coulomb central field (3.182) of an immobile nucleus with charge $+Ze$, the equation may be readily solved exactly⁴⁹ and yields the following spectrum of (doubly-degenerate) energy levels:

$$E = mc^2 \left(1 + \frac{Z^2 \alpha^2}{\lambda^2} \right)^{-1/2}, \quad \text{with } \lambda \equiv n + \left[\left(l + \frac{1}{2} \right)^2 - Z^2 \alpha^2 \right]^{1/2} - \left(l + \frac{1}{2} \right), \quad (9.91)$$

where $n = 1, 2, \dots$ and $l = 0, 1, \dots, n - 1$ are the same quantum numbers as in the nonrelativistic theory (see Sec. 3.6), and $\alpha \equiv e^2/4\pi\epsilon_0\hbar c \approx 1/137$ is the fine structure constant – see Eq. (6.62). The three leading terms of the Taylor expansion of this result in small parameter $Z\alpha$ are as follows:

$$E \approx mc^2 \left[1 - \frac{Z^2 \alpha^2}{2n^2} - \frac{Z^4 \alpha^4}{2n^4} \left(\frac{n}{l + 1/2} - \frac{3}{4} \right) \right]. \quad (9.92)$$

⁴⁸ After such generalization, Eq. (84) is usually called the *relativistic Schrödinger equation*.

⁴⁹ The task left for the reader.

The first of these terms is just the rest energy of the particle. The second term,

$$E_n = -mc^2 \frac{Z^2 \alpha^2}{2n^2} = -\frac{mZ^2 e^4}{(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{2n^2} = -\frac{E_0}{2n^2}, \quad \text{with } E_0 = Z^2 E_H, \quad (9.93)$$

reproduces the nonrelativistic Bohr's formula (3.191). Finally, the third term,

$$-mc^2 \frac{Z^4 \alpha^4}{2n^4} \left(\frac{n}{l+1/2} - \frac{3}{4} \right) = -\frac{2E_n^2}{mc^2} \left(\frac{n}{l+1/2} - \frac{3}{4} \right), \quad (9.94)$$

is just the kinetic-relativistic contribution (6.52) to the fine structure of the Bohr levels (93). However, as we already know from Sec. 6.3, for a spin- $1/2$ particle such as the electron, the spin-orbit interaction (6.56) gives an additional contribution of the same order to the fine structure, so that the net result, confirmed by experiment, is given by Eq. (6.60), i.e. different from Eq. (94). This is very natural, because the relativistic Schrödinger equation does not have the very notion of spin.

Second, even for massive spinless particles (such as Z^0 bosons), for which this equation is believed to be valid, the most important problems are related to particle interactions at high energies of the order of $\Delta E \sim 2mc^2$ (88) and beyond. Due to possibility of creation and annihilation of particle-antiparticle pairs at such energies, the number of particles participating in such interactions is typically considerable (and variable), and its adequate description of the system is given not by the relativistic Schrödinger equation (which is formulated in single-particle terms), but by the *quantum field theory* - to which I will devote just a few sentences in the very end of this chapter.

9.6. Dirac's theory

The real breakthrough toward the quantum relativistic theory of electrons (and any spin- $1/2$ fermions) was achieved in 1928 by P. A. M. Dirac. For that time, the structure of his theory was highly nontrivial. Namely, while formally preserving, in the coordinate representation, the same Schrödinger-picture equation of quantum dynamics as in the nonrelativistic quantum mechanics,⁵⁰

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi, \quad (9.95)$$

it postulates that wavefunction Ψ is not a scalar complex function of time and coordinates, but a *four-component* column-vector (sometimes called the *bispinor*) of such functions, its Hermitian-conjugate bispinor $\Psi^\dagger$ being a 4-component row-vector of their complex conjugates:

$$\Psi = \begin{pmatrix} \Psi_1(\mathbf{r}, t) \\ \Psi_2(\mathbf{r}, t) \\ \Psi_3(\mathbf{r}, t) \\ \Psi_4(\mathbf{r}, t) \end{pmatrix}, \quad \Psi^\dagger = \left(\Psi_1^*(\mathbf{r}, t) \quad \Psi_2^*(\mathbf{r}, t) \quad \Psi_3^*(\mathbf{r}, t) \quad \Psi_4^*(\mathbf{r}, t) \right), \quad (9.96)$$

⁵⁰ After the “naturally-relativistic” form of the Klein-Gordon equation (84), this apparent return to the nonrelativistic Schrödinger equation may look very counter-intuitive. However, it becomes a bit less surprising taking into account the fact (whose proof is left for the reader) that Eq. (84) may be also recast into form (95) for a *two-component* column-vector (spinor) Ψ , with a Hamiltonian which may be represented by a 2×2 matrix - and hence expressed via the Pauli matrices (4).

and that the Hamiltonian participating in Eq. (95) is a 4×4 matrix in the Hilbert space of bispinors Ψ . For a free particle, the postulated Hamiltonian looks amazingly simple:⁵¹

$$\hat{H} = c\hat{\mathbf{a}} \cdot \hat{\mathbf{p}} + \hat{\beta} mc^2. \quad (9.97)$$

Free-
particle
Hamiltonian

where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the same 3D vector of momentum component operators as in the nonrelativistic case, while operators $\hat{\mathbf{a}}$ and $\hat{\beta}$ may be presented in the following shorthand 2×2 form:

$$\hat{\mathbf{a}} \equiv \begin{pmatrix} 0 & \hat{\boldsymbol{\sigma}} \\ \hat{\boldsymbol{\sigma}} & 0 \end{pmatrix}, \quad \hat{\beta} \equiv \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{I} \end{pmatrix}. \quad (9.98a)$$

Dirac
operators

Operator $\hat{\mathbf{a}}$, composed of the Pauli vector operators $\hat{\boldsymbol{\sigma}}$, is also a vector in the usual 3D space, so that each of its 3 Cartesian components is a 4×4 matrix. The particular form of the 2×2 matrices corresponding to operators $\hat{\boldsymbol{\sigma}}$ and $\hat{I}$ in Eq. (98a) depends on the basis selected for representation of the spin states of the particle; for example, in the standard z -basis, in which the Cartesian components $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$ of $\hat{\boldsymbol{\sigma}}$ are represented by the Pauli matrices (4.105), the full matrix form of Eq. (98a) is

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (9.98b)$$

(According to the second of Eq. (98a), β has this form in any spin basis.) It is straightforward to use Eqs. (98) to verify that matrices α_x , α_y , α_z and β satisfy the following relations:

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1, \quad (9.99)$$

$$\alpha_x \alpha_y + \alpha_y \alpha_x = \alpha_y \alpha_z + \alpha_z \alpha_y = \alpha_z \alpha_x + \alpha_x \alpha_z = \alpha_x \beta + \beta \alpha_x = \alpha_y \beta + \beta \alpha_y = \alpha_z \beta + \beta \alpha_z = 0, \quad (9.100)$$

i.e. anticommute.

Acting essentially as in Sec. 4.1, but using commutation relations (99)-(100), it is straightforward to show that any solution to the Dirac equation obeys the probability conservation law, i.e. the continuity equation (1.52), with the probability density,

⁵¹ Moreover, if the time derivative participating in Eq. (95) and the three coordinate derivatives participating (via the momentum operator) in Eq. (97), are merged into one 4-vector operator $\partial/\partial x_k \equiv \{\nabla, \partial/\partial(ct)\}$, the Dirac equation (95) may be rewritten in an even simpler, manifestly Lorentz-invariant 4-vector form (with the implicit summation over the repeated index $k = 1, \dots, 4$ – see, e.g., EM Sec. 9.4):

$$\left(\hat{\gamma}_k \frac{\partial}{\partial x_k} + \mu \right) \Psi = 0, \quad \text{where } \hat{\boldsymbol{\gamma}} \equiv \{\hat{\gamma}_1, \hat{\gamma}_2, \hat{\gamma}_3\} = \begin{pmatrix} 0 & -i\hat{\boldsymbol{\sigma}} \\ i\hat{\boldsymbol{\sigma}} & 0 \end{pmatrix}, \quad \hat{\gamma}_4 = \hat{\beta},$$

where $\mu \equiv mc/\hbar$ – just as in Eq. (84). Note also that, very counter-intuitively, the Dirac Hamiltonian (97) is *linear* in momentum, while the non-relativistic Hamiltonian of a particle, as well as the relativistic Schrödinger equation, are *quadratic* in $\mathbf{p}$. In my humble opinion, the Dirac theory (including the concept of antiparticles) may compete for the title of the most revolutionary theoretical idea in physics, despite such heavy contenders as the Newton laws, the Maxwell equations, the Einstein's relativity, the Bohr atom, and the Gibbs' statistical distributions.

$$w = \Psi^\dagger \Psi, \quad (9.101)$$

and the probability current,

$$\mathbf{j} = c\Psi^\dagger \hat{\boldsymbol{\alpha}} \Psi, \quad (9.102)$$

looking *almost* as in the nonrelativistic theory – cf. Eqs. (1.22) and (1.47). Note, however, the Hermitian conjugation used in these formulas instead of the complex conjugation, in order to form scalars w, j_x, j_y , and j_z from 4-component vectors (96).

This qualified similarity is extended to the fundamental, plane-wave solutions of the Dirac equations in free space. Indeed, plugging such solution, in the form

$$\Psi = u e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad (9.103)$$

into Eqs. (95) and (97), we get a system of 4 coupled, linear algebraic equations for 4 complex c -number amplitudes $u_{1,2,3,4}$. The condition of their consistency yields the same dispersion relation (87), i.e. the same two-branch diagram shown in Fig. 6, as follows from the Klein-Gordon equation. The difference is that plugging each value of ω , given by Eq. (87), back into the system of equations for amplitudes u , we get two solutions for vector u for each of the energy branches. In the standard spin z -basis they may be presented as:

$$\text{for } E = E_+ > 0: \quad u_{+\uparrow} = c_{+\uparrow} \begin{pmatrix} 1 \\ 0 \\ \frac{cp_z}{E_+ + mc^2} \\ \frac{c(p_x + ip_y)}{E_+ + mc^2} \end{pmatrix}, \quad u_{+\downarrow} = c_{+\downarrow} \begin{pmatrix} 0 \\ 1 \\ \frac{c(p_x - ip_y)}{E_+ + mc^2} \\ \frac{-cp_z}{E_+ + mc^2} \end{pmatrix}, \quad (9.104a)$$

$$\text{for } E = E_- < 0: \quad u_{-\uparrow} = c_{\uparrow} \begin{pmatrix} \frac{cp_z}{E_- - mc^2} \\ \frac{c(p_x + ip_y)}{E_- - mc^2} \\ 1 \\ 0 \end{pmatrix}, \quad u_{-\downarrow} = c_{\downarrow} \begin{pmatrix} \frac{c(p_x - ip_y)}{E_- - mc^2} \\ \frac{-cp_z}{E_- - mc^2} \\ 0 \\ 1 \end{pmatrix}, \quad (9.104b)$$

where c are normalization coefficients.

The simplest interpretation of these solutions is that Eq. (103) with vectors u_+ , given by Eq. (104a), represents a spin- $1/2$ particle (say, an electron), while that with vectors u_- given by Eq. (104b) represents an antiparticle (a positron), and two solutions for each particle correspond to two opposite directions of spin, $\sigma_z = \pm 1$, $S_z = \pm \hbar/2$. This interpretation is indeed solid in the nonrelativistic limit, when two last components of vector (104a) and two first components of vector (104b) are negligibly small:

$$u_{+\uparrow} \rightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad u_{+\downarrow} \rightarrow \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad u_{-\uparrow} \rightarrow \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad u_{-\downarrow} \rightarrow \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \quad \text{at } \frac{p_k}{mc} \rightarrow 0. \quad (9.105)$$

In order to show this, let us use the Dirac equation to calculate the Heisenberg-picture law of time evolution of operators of the Cartesian components of the orbital angular momentum $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$, for example of $L_x = yp_z - zp_y$, taking into account that operators (98a) commute with those of $\mathbf{r}$ and $\mathbf{p}$, and also the Heisenberg commutation relations (2.14):

$$i\hbar \frac{\partial \hat{L}_x}{\partial t} = [\hat{L}_x, \hat{H}] = c\hat{\boldsymbol{\alpha}} \cdot [(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y), \hat{\mathbf{p}}] = -i\hbar c(\hat{\alpha}_z \hat{p}_y - \hat{\alpha}_y \hat{p}_z), \quad (9.106)$$

with similar relations for two other Cartesian components of the operator. Since the right-hand part of these equations is different from zero, the orbital momentum is generally *not* conserved - even for a free particle! Let us, however, consider the following vector operator,

$$\hat{\mathbf{S}} \equiv \frac{\hbar}{2} \begin{pmatrix} \hat{\boldsymbol{\sigma}} & 0 \\ 0 & \hat{\boldsymbol{\sigma}} \end{pmatrix}, \quad (9.107a)$$

Spin
operator
in Dirac's
theory

whose Cartesian components, in the z -basis, are represented by 4×4 matrices

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad (9.107b)$$

and calculate the Heisenberg-picture law of time evolution of these components, for example

$$i\hbar \frac{\partial \hat{S}_x}{\partial t} = [\hat{S}_x, \hat{H}] = c[\hat{S}_x, (\hat{\alpha}_x \hat{p}_x + \hat{\alpha}_y \hat{p}_y + \hat{\alpha}_z \hat{p}_z)] = i\hbar c(\hat{\alpha}_z \hat{p}_y - \hat{\alpha}_y \hat{p}_z). \quad (9.108)$$

A direct calculation of the commutators of matrices (98) and (107) yields

$$[\hat{S}_x, \hat{\alpha}_x] = 0, \quad [\hat{S}_x, \hat{\alpha}_y] = i\hbar \hat{\alpha}_z, \quad [\hat{S}_x, \hat{\alpha}_z] = -i\hbar \hat{\alpha}_y, \quad (9.109)$$

so that we finally get

$$i\hbar \frac{\partial \hat{S}_x}{\partial t} = i\hbar c(\hat{\alpha}_z \hat{p}_y - \hat{\alpha}_y \hat{p}_z), \quad (9.110)$$

with similar expressions for other two components of the operator. Comparing this result with Eq. (106), we see that any Cartesian component of operator (5.198),

$$\hat{\mathbf{J}} \equiv \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (9.111)$$

is an integral of motion,⁵² so that this operator may be interpreted as the one presenting the total angular momentum. Hence, operator (104) may be interpreted as the spin operator of a spin- $\frac{1}{2}$ particle (e.g., electron). As it follows from the last of Eq. (107b), columns (105) represent the eigenkets of the z -component of that operator, with eigenstates $S_z = \pm\hbar/2$, depending on the arrow index. So, the Dirac theory provides a justification for spin- $\frac{1}{2}$ – or, somewhat more humbly, replaces the spin hypothesis by an assumption of a simpler (and hence more plausible), Lorentz-invariant Hamiltonian (97).

Note, however, that this fact is not true for the exact solutions (103)-(104), so that generally the eigenstates of the Dirac Hamiltonian are certain linear (coherent) superpositions of component wavefunctions describing the particle and its antiparticle – each with both directions of spin. This fact leads to several interesting effects, including the so-called *Klien paradox* at reflection of a particle from a tunnel barrier.⁵³ It is curious that some of these effects may be reproduced in such nonrelativistic systems as electron moving in a 2D honeycomb lattice (e.g., in graphene), since they also feature a (locally) linear dispersion relation – see Eq. (3.122).⁵⁴

9.7. Low-energy limit

The generalization of the Dirac's theory to the case of a particle with electric charge q , moving in a classically-described electromagnetic field may be obtained using the same Eqs. (90). As a result, Eq. (95) becomes

Dirac equation
with EM field

$$\left[c\hat{\boldsymbol{\alpha}} \cdot (-i\hbar\nabla - q\mathbf{A}) + mc^2\hat{\beta} + (q\phi - \hat{H}) \right] \Psi = 0, \quad (9.112)$$

where the Hamiltonian operator $\hat{H}$ is understood in the sense of Eq. (95), i.e. as the partial time derivative with multiplier $i\hbar$. Let us prepare this equation for a low-energy approximation by acting on its left-hand part by a similar square bracket (also an operator!), but with the opposite sign before the last parentheses. Using relations (99) and (100), and the fact that space- and time-independent operators $\hat{\boldsymbol{\alpha}}$ and $\hat{\beta}$ commute with the spin-independent functions $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$, as well as with the Hamiltonian operator $i\hbar\partial/\partial t$, the result is

$$\left\{ c^2 [\hat{\boldsymbol{\alpha}} \cdot (-i\hbar\nabla - q\mathbf{A})]^2 + (mc^2)^2 - c [\hat{\boldsymbol{\alpha}} \cdot (-i\hbar\nabla - q\mathbf{A}), (q\phi - \hat{H})] - (q\phi - \hat{H})^2 \right\} \Psi = 0. \quad (9.113)$$

A direct calculation of the first square bracket, using Eqs. (98) and (107), yields

$$[\hat{\boldsymbol{\alpha}} \cdot (-i\hbar\nabla - q\mathbf{A})]^2 = (-i\hbar\nabla - q\mathbf{A})^2 - 2q\hat{\mathbf{S}} \cdot \nabla \times \mathbf{A}. \quad (9.114)$$

But according to the last of Eqs. (3.21), the last vector product in the right-hand part is just the magnetic field

$$\mathcal{B} = \nabla \times \mathbf{A}. \quad (9.115)$$

Similarly, we may use the first of Eqs. (3.21), for the electric field,

$$\mathcal{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad (9.116)$$

⁵² It is straightforward to show that this result remains valid for a particle in the field of central potential $U(\mathbf{r})$.

⁵³ See, e.g., A. Calogeracos and N. Dombey, *Contemp. Phys.* **40**, 313 (1999).

⁵⁴ For a review see, e.g., T. Robinson, *Am. J. Phys.* **80**, 141 (2012).

to simplify the commutator participating in Eq. (9.113):

$$\left[\hat{\mathbf{a}} \cdot (-i\hbar\nabla - q\mathbf{A}), (q\phi - \hat{H}) \right] = -q\hat{\mathbf{a}} \cdot [\hat{H}, \mathbf{A}] - i\hbar q \hat{\mathbf{a}} \cdot [\nabla, \phi] = -i\hbar q \frac{\partial \mathbf{A}}{\partial t} - i\hbar \hat{\mathbf{a}} \cdot \nabla \phi = i\hbar q \hat{\mathbf{a}} \cdot \mathcal{E}. \quad (9.117)$$

As a result, Eq. (110) becomes

$$\left\{ c^2 (-i\hbar\nabla - q\mathbf{A})^2 + (q\phi - \hat{H})^2 - (mc^2)^2 - 2qc^2 \hat{\mathbf{S}} \cdot \mathcal{B} + i\hbar c q \hat{\mathbf{a}} \cdot \mathcal{E} \right\} \Psi = 0. \quad (9.118)$$

So far, this is an exact result, equivalent to Eq. (112), but more convenient for an analysis of the low-energy limit in that not only the offset energy $E - mc^2$ (which is the energy used in nonrelativistic quantum mechanics), but also the electrostatic energy of the particle, $|q\langle\phi\rangle|$, are much smaller than the rest energy mc^2 . In this limit, the second and third terms of Eq. (118) almost cancel, and introducing the offset Hamiltonian

$$\hat{\tilde{H}} \equiv \hat{H} - mc^2 \hat{I}. \quad (9.119)$$

we may approximate their difference, up to the first nonvanishing term, as

$$(q\phi \hat{I} - \hat{H})^2 - (mc^2)^2 \hat{I} \equiv (q\phi \hat{I} - mc^2 \hat{I} - \hat{\tilde{H}})^2 - (mc^2)^2 \hat{I} \approx 2mc^2 (\hat{\tilde{H}} - q\phi \hat{I}). \quad (9.120)$$

As a result, after division of all terms by $2mc^2$, Eq. (118) may be approximated as

$$\hat{\tilde{H}}\Psi = \left[\frac{1}{2m} (-i\hbar\nabla - q\mathbf{A})^2 + q\phi - \frac{q}{m} \hat{\mathbf{S}} \cdot \mathcal{B} + \frac{i\hbar q}{2mc} \hat{\mathbf{a}} \cdot \mathcal{E} \right] \Psi. \quad (9.121)$$

Low-energy
Hamiltonian

Let us discuss this important result. The first two terms in the square brackets give the Hamiltonian (3.26) that was extensively used in Chapter 3 for the discussion of nonrelativistic motion of charged particles. Note again that the contribution of the vector-potential $\mathbf{A}$ into that Hamiltonian is essentially *relativistic*, in the following sense: when used for the description of magnetic interaction of two charged particles, due to their orbital motion with speed $v \ll c$, the magnetic interaction is a factor of $(v/c)^2$ smaller than the electrostatic interaction of the particles.⁵⁵ The reason why we did discuss the effects of $\mathbf{A}$ in Chapter 3 was that it was used there to describe *external* magnetic fields, keeping our analysis valid even for the cases when that field is strong by being produced by relativistic effects – such as aligned spins in a permanent magnet.

The next, third term in the square brackets is also familiar to the reader: it was introduced informally in Sec. 4.1, and then formally in Sec. 4.4 to describe the effect of magnetic field on particle's spin – see Eqs. (4.3), (4.5), and (4.163). When justifying this form of interaction, I referred mostly to results of Stern-Gerlach-type experiments, but it is extremely pleasing that this result⁵⁶ follows from such a fundamental relativistic treatment as Dirac's theory. As we already know from the discussion of

⁵⁵ This difference may be traced even by classical means – see, e.g., EM Sec. 5.1.

⁵⁶ With the g -factor still equal to exactly 2 – see Eq. (4.116) and its discussion. In order to describe the small deviation of g_e from 2, the electromagnetic field should be quantized (just as this was done in Secs. 1-4), and its potentials $\mathbf{A}$ and ϕ , participating in Eq. (112) should be treated as operators – rather than as c -number functions as was assumed above. The calculation of this deviation is one of the basic problems of quantum field theory. Other small but important effects of electromagnetic interactions, described by the theory, include the so-called *Lamb shift* of atomic levels – see the end of this chapter for references.

the Zeeman effect in Sec. 6.4, the effects of magnetic field on the orbital motion of an electron (described by orbital angular momentum $\mathbf{L}$) and its spin $\mathbf{S}$ are of the same order, i.e. present an essentially relativistic effect.

Finally, the last term in the square brackets of Eq. (121) is also not quite new for us: in particular it describes the spin-orbit interaction. Indeed, in the case of classical, spherical-symmetric electric field $\mathcal{E}$ with potential $\phi(r) = U(r)/q$, the term may be reduced to Eq. (6.56b):

Spin-orbit
coupling

$$\hat{H}_{\text{so}} = \frac{1}{2m^2c^2} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \frac{1}{r} \frac{dU}{dr} = -\frac{q}{2m^2c^2} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \frac{1}{r} \mathcal{E}. \quad (9.122)$$

The proof of this correspondence requires a bit of additional work,⁵⁷ because in Eq. (121), the term responsible for the spin-orbit interaction acts on 4-component wavefunctions, while Hamiltonian (122) is supposed to act on nonrelativistic wavefunctions with account of spin, whose coordinate representation is given by 2-component columns – *spinors*:⁵⁸

$$\psi = \begin{pmatrix} \psi_{\uparrow} \\ \psi_{\downarrow} \end{pmatrix}. \quad (9.123)$$

The simplest way to prove the identity of the two formulas is not to use Eq. (121) directly, but to return to the Dirac equation (112), for the particular case of motion in a stationary electric field with no magnetic field, when Dirac's Hamiltonian is reduced to

$$\hat{H} = c\hat{\boldsymbol{\alpha}} \cdot \hat{\mathbf{p}} + \hat{\beta} mc^2 + U(\mathbf{r}). \quad (9.124)$$

Since this Hamiltonian is time-independent, we may look for its 4-component eigenfunctions in the form

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \psi_+(\mathbf{r}) \\ \psi_-(\mathbf{r}) \end{pmatrix} \exp\left(-i \frac{E}{\hbar} t\right), \quad (9.125)$$

where each of $\psi_{\pm}$ is a 2-component column of the type (123), representing two spin states of the particle (index +) and antiparticle (index -). Plugging Eq. (125) into Eq. (124), and using Eq. (98a), we get the following system of two linear equations:

$$\begin{aligned} [E - mc^2 - U(\mathbf{r})]\psi_+ - c\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}\psi_- &= 0, \\ [E + mc^2 - U(\mathbf{r})]\psi_- - c\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}\psi_+ &= 0. \end{aligned} \quad (9.126)$$

⁵⁷ The only facts immediately evident from Eq. (121) are that the term we are discussing is proportional to the electric field, as required by Eq. (122), and that it is of the proper order of magnitude. Indeed, Eqs. (101)-(102) imply that in the Dirac theory, $c\hat{\boldsymbol{\alpha}}$ plays the role of the velocity operator, so that the expectation values of the term are of the order of $\hbar qv\mathcal{E}/2mc^2$. Since the expectation values of the operators participating in Hamiltonian (122) scale as $S \sim \hbar/2$ and $L \sim mvr$, the spin-orbit interaction energy has the same order of magnitude.

⁵⁸ As a reminder, in this course the notion of spinor was introduced earlier for two-particle states - see Eq. (8.14). For a single particle, that definition is reduced to $\psi(\mathbf{r})|s\rangle$, whose representation in a particular spin-1/2 basis is a column similar to Eq. (123). Also note that spinors (123) may be expanded into a series over the spin-orbitals (8.117) discussed in Sec. 8.3, with index j used for numbering both the two directions of spin (i.e. two components of spinor's column) and orbital eigenfunctions.

Expressing ψ from the latter equation, and plugging the result into the former one, we get the following single equation for particle's spinor:

$$\left[E - mc^2 - U(\mathbf{r}) - c^2 \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \frac{1}{E + mc^2 - U(\mathbf{r})} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \right] \psi_+ = 0. \quad (9.127)$$

So far, this is an exact equation for eigenstates and eigenvalues of Hamiltonian (124). It may be substantially simplified in the low-energy limit when both the potential energy⁵⁹ and the nonrelativistic eigenenergy

$$\tilde{E} \equiv E - mc^2 \quad (9.128)$$

are much less than mc^2 . Indeed, in this case the expression in denominator of the last term in the brackets of Eq. (127) is close to $2mc^2$. Since $\boldsymbol{\sigma}^2 = 1$, with that replacement, Eq. (127) is reduced to the nonrelativistic Schrödinger equation, similar for both spin components of ψ_+ , and hence giving spin-degenerate energy levels. In order to recover small relativistic and spin-orbit effects, we need a slightly more accurate approximation:

$$\frac{1}{E + mc^2 - U(\mathbf{r})} \equiv \frac{1}{2mc^2 + \tilde{E} - U(\mathbf{r})} = \frac{1}{2mc^2} \left[1 + \frac{\tilde{E} - U(\mathbf{r})}{2mc^2} \right]^{-1} \approx \frac{1}{2mc^2} \left[1 - \frac{\tilde{E} - U(\mathbf{r})}{2mc^2} \right], \quad (9.129)$$

in which Eq. (127) is reduced to

$$\left[\tilde{E} - U(\mathbf{r}) - \frac{\hat{\mathbf{p}}^2}{2m} + \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \frac{\tilde{E} - U(\mathbf{r})}{(2mc^2)^2} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \right] \psi_+ = 0. \quad (9.130)$$

As follows from Eqs. (5.46)-(5.47), the operators of momentum and of a function of coordinates commute as

$$[\hat{\mathbf{p}}, U(\mathbf{r})] = -i\hbar \nabla U, \quad (9.131)$$

so that the last term in square brackets of Eq. (130) may be rewritten as

$$\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \frac{\tilde{E} - U(\mathbf{r})}{(2mc)^2} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} = \frac{\tilde{E} - U(\mathbf{r})}{(2mc)^2} \hat{\mathbf{p}}^2 - \frac{i\hbar}{(2mc)^2} (\hat{\boldsymbol{\sigma}} \cdot \nabla U)(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}). \quad (9.132)$$

Since in the low-energy limit both terms in the right-hand part of this relation are much smaller than the three leading terms of Eq. (130), in the first of them we may replace the nominator with its non-relativistic value $\hat{\mathbf{p}}^2 / 2m$. With this replacement, the term coincides with the first relativistic correction to the kinetic energy operator – see Eqs. (6.47) and (6.49a). The second term, proportional to the electric field $\boldsymbol{\mathcal{E}} = -\nabla\phi = -\nabla U/q$, may be transformed further on, using a readily verifiable relation

$$(\hat{\boldsymbol{\sigma}} \cdot \nabla U)(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}) = (\nabla U) \cdot \hat{\mathbf{p}} + i\hat{\boldsymbol{\sigma}} \cdot [(\nabla U) \times \hat{\mathbf{p}}]. \quad (9.133)$$

Of the two terms in the right-hand part, only the second one depends on spin,⁶⁰ giving the following spin-orbital interaction contribution to the Hamiltonian,

⁵⁹ Strictly speaking, this requirement is imposed on the expectation values of $U(\mathbf{r})$ in the eigenstates to be found.

$$\hat{H}_{\text{so}} = \frac{\hbar}{(2mc)^2} \hat{\mathbf{g}} \cdot [(\nabla U) \times \hat{\mathbf{p}}] = \frac{q}{2m^2 c^2} \hat{\mathbf{S}} \cdot [(\nabla \phi) \times \hat{\mathbf{p}}]. \quad (9.134)$$

For a central electric field with $\phi(\mathbf{r}) = \phi(r)$, the potential gradient has only one, radial component: $\nabla \phi = (d\phi/dr)\mathbf{r}/r = -\mathcal{E}\mathbf{r}/r$, and with the angular momentum definition $\hat{\mathbf{L}} \equiv \mathbf{r} \times \hat{\mathbf{p}}$, Eq. (134) is reduced to Eq. (122).

As was shown in Sec. 6.3, the perturbative treatment of Eq. (122), together with the kinetic-relativistic correction (6.49), in the hydrogen-like atom problem, leads to the fine structure of each Bohr level E_n , given by Eq. (6.60):

$$\Delta E_{\text{so}} = -\frac{2E_n}{mc^2} \left(3 - \frac{4n}{j+1/2} \right). \quad (9.135)$$

This result gets a confirmation from the surprising fact that for the hydrogen-like atom problem, the Dirac equation may be solved *exactly* – without any assumptions. I do not have time/space to reproduce the solution,⁶¹ and will list just the final result for the energy spectrum:

H-like
atom's
eigenenergies

$$\frac{E}{mc^2} = \left\{ 1 + \frac{Z^2 \alpha^2}{\left[n + \left\{ (j+1/2)^2 - Z^2 \alpha^2 \right\}^{1/2} - (j+1/2) \right]^2} \right\}^{-1/2}. \quad (9.136)$$

Here $n = 1, 2, \dots$ is the same main quantum number as in Bohr's theory, while j is the quantum number specifying eigenvalues (5.203) of the total angular momentum's square J^2 in the units of $\hbar^2$, taking half-integer values: $j = l \pm 1/2 = 1/2, 3/2, 5/2, \dots$ - see Eq. (5.215). Such set of quantum numbers is rather natural, because due to the spin-orbit interaction, the orbital and spin angular momenta are not conserved, while their vector sum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, is - in the absence of external magnetic field. Each energy level (136) is doubly-degenerate, with two eigenstates representing two directions of spin – i.e. two values of $l = j \mp 1/2$ at fixed j .

Since according to Eq. (1.9), the square of the fine-structure constant $\alpha \equiv e^2/4\pi\epsilon_0\hbar c$ may be presented as the ratio E_H/mc^2 , the low-energy limit ($E - mc^2 \sim E_H \ll mc^2$) may be pursued by expanding Eq. (136) into the Taylor series in $(Z\alpha)^2 \ll 1$. The result,

$$E \approx mc^2 \left[1 - \frac{Z^2 \alpha^2}{2n^2} - \frac{Z^4 \alpha^4}{2n^4} \left(\frac{n}{|j+1/2|} - \frac{3}{4} \right) \right], \quad (9.137)$$

has the same structure, and allows the same interpretation as Eq. (92), but with the last term coinciding with Eq. (6.52) - and with experimental results. Historically, this correct description of the fine structure of atomic levels provided a decisive proof of Dirac's theory.

However, even such an impressive theory does not have too many direct applications. The main reason for that was already discussed in brief in the end of Sec. 5: due to the possibility of creation and

⁶⁰ The first term gives a small, spin-independent shift of the energy spectrum, which is very difficult to verify experimentally.

⁶¹ Good descriptions of the solution are available in many textbooks (the older the better :-), for example see Sec. 53 in L. Schiff, *Quantum Mechanics*, 3rd ed., McGraw-Hill (1968).

annihilation of particle-antiparticle pairs at energies higher than $2mc^2$, the number of particles participating in high-energy interactions is not fixed. An adequate general description of such situation is given by the quantum field theory, in which the particle wavefunction is treated as a field to be quantized, using so-called *field operators* $\hat{\Psi}(\mathbf{r}, t)$ – very much as the electromagnetic field was treated in Secs. 1-4 above. (The Dirac equation follows from the quantum field theory in the single-particle approximation.)

As was mentioned above on several occasions, the quantum field theory is beyond the scope of this course, and I have to stop here, referring the interested reader to one of several excellent available textbooks on this discipline.⁶² (I would strongly encourage the student going in this direction to start with playing with the field operators on this or her own, taking clues from Eqs. (16), but replacing the creation / annihilations operators $\hat{a}_j^\dagger$ and $\hat{a}_j$ of the harmonic oscillator with those of the general second quantization formalism outlined in Sec. 8.3.)

9.8. Exercise problems

9.1.* Prove the Casimir formula (23) for the attraction force $F = -PA$ between two perfectly conducting parallel plates of area A , separated by a narrow vacuum gap $d \ll A^{1/2}$.

Hint: You may like to use the *Euler-Maclaurin formula*.⁶³

9.2. Radiation of some single-mode quantum sources may have such a high degree of coherence that it is possible to observe interference from two independent sources with virtually the same frequency, incident on one detector.

(i) Generalize Eq. (29) to this case.

(ii) Use the generalized expression to show that incident waves in different Fock states do not create an interference pattern.

9.3. Calculate the zero-delay value $g^{(2)}(0)$ of the second-order correlation function of a single-mode electromagnetic field in the so-called *Schrödinger-cat state*: a coherent superposition of two Glauber states, with equal amplitudes, equal but sign-opposite parameters α , and a certain phase shift between them.

9.4. Calculate the zero-delay value $g^{(2)}(0)$ of the second-order correlation function of single-mode electromagnetic field in the squeezed ground state ν defined by Eq. (5.172).

9.5. Calculate the rate of spontaneous photon emission (into the unrestricted free space) by a hydrogen atom, initially in the $2p$ state ($n = 2$, $l = 1$) with $m = 0$. Would the result be different for $m = \pm$

⁶² For a gradual introduction see, e.g., either L. Brown, *Quantum Field Theory*, Cambridge U. Press (1994) or R. Klauber, *Student Friendly Quantum Field Theory*, Sandtrove (2013); on the other hand, M. Srednicki, *Quantum Field Theory*, Cambridge U. Press (2007) and A. Zee, *Quantum Field Theory in a Nutshell*, 2nd ed., Princeton (2010), among many others, offer a steeper learning curve.

⁶³ See, e.g., MA Eq. (2.12).

1? for the $2s$ state ($n = 2, l = 0, m = 0$)? Discuss the relation between these quantum-mechanical results and those given by the classical theory of radiation, using the simplest classical model of the atom.

9.6. An electron has been placed at the lowest excited level of a spherically-symmetric, quadratic potential well $U(\mathbf{r}) = m_e \omega^2 r^2 / 2$. Calculate the rate of its relaxation to the ground state, with emission of a photon (to the free space). Compare the rate with that for a similar transition of the hydrogen atom, for the case when the radiation frequencies of these two systems are equal.

9.7. Derive an analog of Eq. (53) for the spontaneous photon emission into the free space, due to a change of its *magnetic* dipole moment $\mathbf{m}$ of a small-size system.

9.8. A spin- $1/2$ particle, with the gyromagnetic ratio γ , is in its orbital ground state in a dc magnetic field $\mathcal{B}_0$. Calculate the rate of its spontaneous transition from the higher to the lower energy level, with the emission of a photon into the free space. Evaluate the rate for an electron in a field of 10 T, and discuss the implications of this result for experiments with electron spins.

9.9. Calculate the rate of spontaneous transitions between the two sublevels of the ground state of a hydrogen atom, formed as a result of its hyperfine splitting. Discuss the implications of the result for the width of the 21-cm spectral line.

9.10. Find the eigenstates and eigenvalues of the Janes-Cummings Hamiltonian (78), and discuss their behavior near the resonance point $\omega = \Omega$.

9.11. Analyze the Purcell effect, mentioned in Secs. 3 and 4, qualitatively; in particular, calculate the so-called *Purcell factor* F_P , defined as the ratio of the spontaneous emission rates Γ_s of an atom in a resonant cavity (tuned exactly to the quantum transition frequency) and that in the free space.

9.12. Prove that the Klein-Gordon equation (9.84) may be rewritten in the form similar to the nonrelativistic Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi,$$

for a two-component wavefunction ψ ,⁶⁴ with the Hamiltonian represented (in the usual z -basis) by the following 2×2 -matrix:

$$H = -(\sigma_z + i\sigma_y) \frac{\hbar^2}{2m} \nabla^2 + mc^2 \sigma_z.$$

Use your solution to discuss the physical meaning of the wavefunction's components.

9.13. Calculate and discuss the energy spectrum of a relativistic, spinless, charged particle placed into an external uniform, time-independent magnetic field $\mathcal{B}$. Use the result to formulate the condition of validity of the nonrelativistic theory.

⁶⁴ Here ψ is a function of both $\mathbf{r}$ and t , and the lower-case letter is used only to distinguish this two-component spinor from the scalar function $\Psi(\mathbf{r}, t)$ obeying the Klein-Gordon equation.

Hint: Reduce the relativistic Schrödinger equation, describing the problem, to the nonrelativistic one describing the same problem, with some effective parameter(s).

9.14. Prove Eq. (91) for the energy spectrum of a hydrogen-like atom, calculated from the relativistic Schrödinger equation.

Hint: Use the fact that, as a mathematical analysis of Eq. (3.184) shows, its eigenvalues are given by Eq. (3.191), $\varepsilon_n = -1/2n^2$, with $n = l + 1 + n_r$, where $n_r = 0, 1, 2, \dots$, even if l is not integer.⁶⁵

9.15. Derive the general expression for the differential cross-section of the elastic scattering of a spinless relativistic particle by a static potential $U(\mathbf{r})$, in the Born approximation, and formulate the conditions of its validity. Use these results to calculate the differential cross-section of scattering of a particle with electric charge $-e$ by the Coulomb electrostatic potential $\phi(\mathbf{r}) = Ze/4\pi\epsilon_0 r$.

9.16. Calculate the commutator of operator $\hat{L}^2$ and the Dirac Hamiltonian of a free particle. Compare the result with that for the nonrelativistic Hamiltonian of a free particle, and interpret the difference.

9.17.* In the Heisenberg picture of quantum dynamics, derive an equation describing time evolution of free electron's velocity in the Dirac theory. Solve the equation for the simplest state, with constant energy and momentum, and discuss the solution.

9.18.* Calculate the eigenstates and eigenenergies of a spin- $1/2$ particle with charge q , placed into a uniform, time-independent external magnetic field $\mathcal{B}$. Compare the calculated energy spectrum with those following from the non-relativistic theory and the relativistic Schrödinger equation.

9.19.* Following the recommendation in the end of Chapter 9 of the lecture notes, introduce the quantum field operators $\hat{\psi}$, which would be related to the usual wavefunctions ψ just as the EM field operators (9.16) are related to the classical electromagnetic fields, and explore the basic properties of these operators. (For this preliminary study, consider just the fixed-time situation.)

⁶⁵ Actually, the key relation (3.192), $n \geq l + 1$, mathematically stems from the fact that the “genuine” quantum number of the radial problem, n_r , can only take non-negative integer values.

Chapter 10. Making Sense of Quantum Mechanics

This (very cryptic) chapter addresses the issues of quantum mechanics interpretation that are still a subject of debate – fortunately not affecting practical applications of the quantum theory.

10.1. Hidden variables and local reality

Only now, with a quantitative understanding of the principles of quantum mechanics, we are ready to proceed to the discussion of its interpretation¹ – the issue which is very closely related to problems of measurements, already discussed in Sec. 7.7. As was already mentioned in that section, the founding fathers of quantum mechanics have not left much guidance on these topics, because in the first years after the advent of this exciting new theory they gave understandable preference to using it for deriving new particular results, and then were much distracted by the development of nuclear physics and its applications. This is why, after a very important but inconclusive discussion between A. Einstein and N. Bohr in the mid-30s, the debates of quantum measurements and the related conceptual issues of quantum mechanics have resumed only in the 1950s. They have led to a key contribution by J. Bell in the early 1960s, and an important experimental work on verifying Bell's inequalities (see below), but besides that work, the recent progress is marginal, and opinions of even prominent physicists on certain issues are still very much different.

Perhaps the central controversial issue is question (iii) posed in Sec. 7.7: what (if any :-) is the “real” state of a quantum-mechanical system *before* a nearly-perfect measurement giving a certain outcome? In order to be specific, let us focus again on the simplest example of Stern-Gerlach measurements of spin- $\frac{1}{2}$ particles - because of their physical transparency and technical simplicity.² As the reader knows very well by now, even in a pure quantum spin state (for example, $\uparrow$), i.e. the least uncertain state of the system, the results of the Stern-Gerlach measurements of other spin component are still uncertain. Indeed, as we know from Sec. 4.4, the ket-vector of this state may be presented as

$$|\uparrow\rangle = \frac{1}{\sqrt{2}}(|\rightarrow\rangle + |\leftarrow\rangle), \quad (10.1)$$

so that the probabilities of measuring any of values $S_x = +\hbar/2$ and $S_x = -\hbar/2$ equal 50%. So, has the spin had a certain value of S_x a split second *before* the Stern-Gerlach measurement that gave a certain outcome, for example $S_x = +\hbar/2$? For a classical system, with perfect detectors, the answer is definitely yes. In this case, the pre-measurement probability of 50% just reflects the degree of our ignorance about the real state of the system, and the detector merely *reveals* it.

However, the situation in quantum mechanics is different, and such interpretation is impossible, as was clearly shown in the famous *EPR paper* published in 1935 by A. Einstein, B. Podolsky, and N.

¹ I believe that another popular name for this group of issues, “foundations of quantum mechanics”, is hardly appropriate. The only reliable foundation of physics (or any other genuine scientific discipline) is a set of experimental facts.

² As was discussed in Sec. 7.7, Stern-Gerlach-type experiments may be readily made almost “perfect”, i.e. virtually unaffected by instrument imperfections, provided that we do not care about the state of the particle *after* a single-shot measurement.

Rosen. Its original discussed thought experiments with a pair of 1D particles prepared in a quantum state in that both the *sum* of their momenta and *difference* of their coordinates are exactly fixed: $p_1 + p_2 = 0$, $x_1 - x_2 = a$.³ However, usually the discussion is recast into an equivalent Stern-Gerlach experiment shown in Fig. 1a.⁴ A source emits rare pairs of spin- $\frac{1}{2}$ particles, propagating in opposite directions, with exactly zero net spin, but otherwise in random spin states. After the spatial separation of the particles has become sufficiently large (see below), the spin state of each of them is measured with a Stern-Gerlach detector, one of them (Fig. 1, detector SG₁) somewhat closer to the particle source, so it makes the measurement first, at time $t_1 < t_2$.

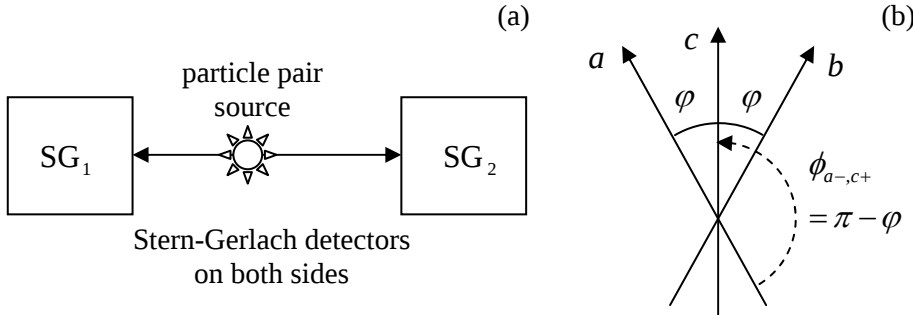


Fig. 10. 1. (a) General scheme of two-particle Stern-Gerlach experiments, and (b) the orientation of the detectors, assumed at the derivation of Bell's inequality (14).

First, let the detectors be oriented say along the same direction, say axis z . Evidently, the probability of each detector to give any of values $S_z = \pm\hbar/2$ is 50%. However, if the first detector had given result $S_z = -\hbar/2$, even before the second detector's measurement, we know that it will give result $S_z = +\hbar/2$ with 100% probability. So far, the result allows for a classical interpretation, just for the single-particle measurements discussed in Secs. 2.5 and 7.7. Thus we may fancy that the second particle really has a definite spin before the measurement, and the first measurement has just removes our ignorance about that reality. In other words, the change of probability is due to the statistical ensemble redefinition: the 50% probability belongs to the ensemble of all experiments, while the 100% probability, to the sub-ensemble of experiments with the $S_z = -\hbar/2$ outcome of the first experiment.

However, let the source generate the particle pairs in the entangled, singlet state (8.19),

$$|s_{12}\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \quad (10.2)$$

that certainly satisfies the above assumptions: the probability of each S_z value of any particle is 50%, the sum of both S_z is exactly zero, and if the first detector's result is $S_z = -\hbar/2$, then the state of the remaining particle is $\uparrow$, with zero uncertainty. Now let us use Eq. (1), and its counterpart for vector $|\downarrow\rangle$,⁵ to present the same initial state (2) in the form

³ This is possible, because the corresponding operators commute: $[\hat{p}_1 - \hat{p}_2, \hat{x}_1 + \hat{x}_2] = [\hat{p}_1, \hat{x}_1] - [\hat{p}_2, \hat{x}_2] = 0$.

⁴ Another convenient experimental technique of entangled state generation, frequently used in this field, is the *four-wave mixing* (FWM) of optical photons. Its brief discussion may be found, for example, in CM Sec. 5.5.

⁵ As a reminder, it differs from Eq. (1) only by the sign in the parentheses - see, e.g., Eqs. (4.123).

$$|s_{12}\rangle = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} (|\rightarrow\rangle + |\leftarrow\rangle) \frac{1}{\sqrt{2}} (|\rightarrow\rangle - |\leftarrow\rangle) - \frac{1}{\sqrt{2}} (|\rightarrow\rangle - |\leftarrow\rangle) \frac{1}{\sqrt{2}} (|\rightarrow\rangle + |\leftarrow\rangle) \right]. \quad (10.3)$$

Opening the parentheses (without swapping the ket-vector order!), we get an expression similar to Eq. (2), but now for the x -basis:

$$|s_{12}\rangle = \frac{1}{\sqrt{2}} (|\rightarrow\leftarrow\rangle - |\leftarrow\rightarrow\rangle). \quad (10.4)$$

Hence if we use the first detector (closest to the particle source) to measure S_x rather than S_z , then after it had given a certain result (say, $S_x = -\hbar/2$), we know for sure, before the second particle spin's measurement, that its S_x component equals $+\hbar/2$.

So, depending on the experiment performed on the first particle, the second particle turns out to be in one of two states - either with a definite component S_z or with a definite component S_x , in each case without any uncertainty. Evidently, this situation cannot be interpreted in classical terms if the particles do not interact during the measurements. A. Einstein was deeply unhappy with such situation, because it did not satisfy the general requirement to any theory, which nowadays is called the *local reality*. His definition of this requirement was as follows:

“The real factual situation of system 2 is independent of what is done with system 1 that is spatially separated from the former”.

(Here the term “separated” in this sentence is a bit uncertain, but from the context it is clear that Einstein meant the detector separation by a *superluminal interval*, i.e. by distance

$$|\mathbf{r}_1 - \mathbf{r}_2| > c|t_1 - t_2|, \quad (10.5)$$

where the measurement time difference, participating in the right-hand part, includes the measurement duration.) In Einstein's view, since quantum mechanics does not satisfy the local reality condition, it cannot be considered a complete theory of Nature.

This situation naturally raises the question whether *something* (usually called *hidden variables*) may be added to the quantum-mechanical description in order to satisfy the local reality requirement. The first definite statement in this regards was J. von Neumann's “proof”⁶ (first famous, then infamous :-)) that such variables cannot be introduced; for a while his work satisfied quantum mechanics practitioners.⁷ A major new contribution to the problem was made only in the 1960s by J. Bell.⁸ First of all, he has found an elementary (in his words, “foolish”) error in von Neumann's logic, which voids his “proof”. Second, he demonstrated that Einstein's local reality condition is *incompatible* with conclusions of quantum mechanics – that had been, by that time, confirmed by too many experiments to be seriously questioned. Since no hidden variable introduction can change this situation, in this sense such introduction is impossible.

⁶ In his pioneering book J. von Neumann, *Mathematische Grundlagen der Quantenmechanik* [Mathematical Foundations of Quantum Mechanics], Springer, 1932. (The first English translation was published only in 1955.)

⁷ Evidently, it would not satisfy A. Einstein, but reportedly he did not know about von Neumann's result before signing the EPR paper.

⁸ See, e. g., J. S. Bell, *Rev. Mod. Phys.* **38**, 447 (1966), or J. S. Bell, *Foundations of Physics* **12**, 158 (1982).

Let me describe a particular version of Bell's proof (suggested by E. Wigner), using the same EPR pair experiment (Fig. 1a), in that each SG detector may be oriented in any of 3 directions: a , b , or c - see Fig. 1b. As we know from Chapter 4, if a fully-polarized beam of spin- $\frac{1}{2}$ particles is passed through a Stern-Gerlach apparatus forming angle ϕ with the polarization axis, the probabilities of two counterpart outcomes of the experiment are

$$W(\phi_+) = \cos^2 \frac{\phi}{2}, \quad W(\phi_-) = \sin^2 \frac{\phi}{2}. \quad (10.6)$$

Quantum-mechanical result for probabilities

Let us use this formula to calculate all joint probabilities of measurement outcomes, starting from the detectors 1 and 2 oriented, respectively, in directions a and c . Since the angle between *negative* direction of axis a and *positive* direction of axis c is $\phi_{a-,c+} = \pi - \phi$ (see the dashed arrow in Fig. 1b), we get

$$W(a_+, c_+) = W(a_+)W(c_+ | a_+) = \frac{1}{2} \cos^2 \frac{\phi_{a-,c+}}{2} = \frac{1}{2} \cos^2 \frac{\pi - \phi}{2} = \frac{1}{2} \sin^2 \frac{\phi}{2}. \quad (10.7)$$

Absolutely similarly,

$$W(c_+, b_+) = W(c_+)W(b_+ | c_+) = \frac{1}{2} \sin^2 \frac{\phi}{2}, \quad (10.8)$$

$$W(a_+, b_+) = W(a_+)W(b_+ | a_+) = \frac{1}{2} \cos^2 \frac{\pi - 2\phi}{2} = \frac{1}{2} \sin^2 \phi. \quad (10.9)$$

Now note that for any angle ϕ smaller than $\pi/2$ (as in the case shown in Fig. 1b),

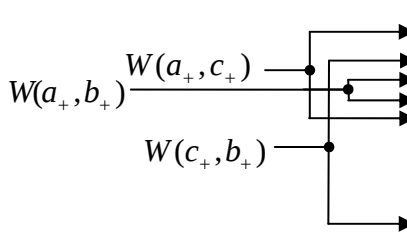
$$\frac{1}{2} \sin^2 \phi \geq \frac{1}{2} \sin^2 \frac{\phi}{2} + \frac{1}{2} \sin^2 \frac{\phi}{2} \equiv \sin^2 \frac{\phi}{2}. \quad (10.10)$$

(For example, for $\phi \rightarrow 0$ the left-hand part of this relation tends to $\phi^2/2$, while the right-hand part, to $\phi^2/4$.) Hence the quantum-mechanical result gives, in particular,

$$W(a_+, b_+) \geq W(a_+, c_+) + W(c_+, b_+), \quad \text{for } |\phi| \leq \pi/2. \quad (10.11)$$

Quantum-mechanical result for joint probabilities

On the other hand, we may compose another inequality for the same probabilities without calculating them from any particular theory, but using the local reality assumption. Let us list all possible outcomes of detector measurements, taking into account the zero net spin:



Detector 1 results	Detector 2 results	Probability
a_+, b_+, c_+	a_-, b_-, c_-	W_1
a_+, b_+, c_-	a_-, b_-, c_+	W_2
a_+, b_-, c_+	a_-, b_+, c_-	W_3
a_+, b_-, c_-	a_-, b_+, c_+	W_4
a_-, b_+, c_+	a_+, b_-, c_-	W_5
a_-, b_+, c_-	a_+, b_-, c_+	W_6
a_-, b_-, c_+	a_+, b_+, c_-	W_7
a_-, b_-, c_-	a_+, b_+, c_+	W_8

From the local reality point of view, these measurement options are independent, so we may write:

$$W(a_+, c_+) = W_2 + W_4, \quad W(c_+, b_+) = W_3 + W_7, \quad W(a_+, b_+) = W_3 + W_4. \quad (10.12)$$

On the other hand, since no probability may be negative (by its very definition), we may always write

$$W_3 + W_4 \leq (W_2 + W_4) + (W_3 + W_7). \quad (10.13)$$

Plugging into this inequality the values of these two parentheses, given by Eq. (12), we get

$$W(a_+, b_+) \leq W(a_+, c_+) + W(c_+, b_+). \quad (10.14)$$

Bell's
inequality for
local-reality
theories

This is (one of several possible forms of) the *Bell's inequality* that has to be satisfied by any local-reality theory; it directly contradicts the quantum-mechanical result (11).

Though experimental tests of the Bell's inequalities had been started in the late 1960s, the interpretation of first results was vulnerable to two criticisms:

(i) The detectors were not fast enough and not far enough to have relation (5) satisfied. This is why, as the matter of principle, there was a chance that information on one measurement had been transferred (by some, mostly implausible) means to particles before the second measurement - the so-called *locality loophole*.

(ii) Particle detection efficiencies were too low to have sufficiently small error bars for both parts of the inequality – the *detection loophole*.

Gradually, these loopholes have been closed.⁹ As expected, substantial violations of Bell inequalities equivalent to Eq. (14) have been proved, essentially rejecting any possibility to reconcile quantum mechanics with Einstein's local reality requirement.

10.2. Interpretations of quantum mechanics

The fact that quantum mechanics is incompatible with local reality, makes its reconciliation with our (classically-bred) “common sense” rather challenging. Here is a brief list of the major interpretations of quantum mechanics, that try to provide at least a partial reconciliation of this kind:

(i) The so-called *Copenhagen interpretation*, to which most physicists subscribe. This “interpretation” does not really interpret anything; it just states the internal randomness of measurement results in quantum mechanics, essentially saying: “Do not worry; this is just how it is; live with it”. For me personally, this interpretation, at least in its most frequently repeated forms, has only one, rather pedagogical weakness: though it implies statistical ensembles (otherwise, how would you define the probability?), but does not put a sufficient emphasis on their role, in particular the possible ensemble

⁹ Important milestones on that way were experiments by A. Aspect *et al.*, *Phys. Rev. Lett.* **49**, 91 (1982) and M. Rowe *et al.*, *Nature* **409**, 791 (2001). A detailed review of the experimental situation was given, for example, by M. Genovese, *Phys. Repts.* **413**, 319 (2005); see also more recent experiments by D. Matsukevich *et al.*, *Phys. Rev. Lett.* **100**, 150404 (2008) and D. Salart *et al.*, *Nature* **454**, 861 (2008). Presently, a low-noise demonstration of the Bell inequality violation has become a standard test in each experiment with entangled qubits used for quantum encryption research – see Sec. 8.5.

redefinition as the only key point of human involvement in the measurement process.¹⁰ Perhaps the most impressive objection to the Copenhagen interpretation was given by A. Einstein during his 1935 discussion with N. Bohr: “God does not play dice.” OK, when Einstein speaks, we all should listen, but perhaps when God speaks (through the experimental results), we have to pay even more attention.

(ii) *Non-local reality*. After the dismissal of von Neumann’s “proof” by J. Bell, to the best of my knowledge, there has been *no* proof that hidden parameters *could not* be introduced, provided that they do not imply the local reality. Of constructive approaches, perhaps the most notable contribution was made by D. Bohm¹¹ who developed the L. de Broglie’s interpretation of the wavefunction as a “pilot wave”, making it quantitative. In the wave mechanics version of this concept, the wavefunction, governed by the Schrödinger equation, just guides a real, point-like classical particle whose coordinates serve as hidden variables. However, this concept does not satisfy the notion of local reality. Namely, the measurement of particle’s coordinate at a certain point $\mathbf{r}_1$ has to *instantly* change the wavefunction everywhere, including points $\mathbf{r}_2$ in the superluminal interval range (4). So, Bohm’s hidden variables would hardly make A. Einstein happy. After having recognized this problem, D. Bohm abandoned his theory – in J. Bell’s view, perhaps too early. In my personal taste, however, the assumption of such (in Einstein’s words) “spooky action at a distance” is too large a sacrifice to save the classical determinism.

(iii) The *many-world interpretation* introduced in 1957 by H. Everett and popularized in the 1960s and 1970s by B. de Witt. In this interpretation, *all* possible measurement outcomes *do* happen, splitting the Universe into the corresponding number of “parallel” Universes, so that from one of them, other Universes and hence other outcomes cannot be observed. Let me leave to the reader an estimate of the rate at which the parallel Universes being constantly generated (say, per second), taking into account that such generation should take place not only at explicit lab experiments, but at any irreversible process such as fission of any atom nucleus or absorption of a photon, everywhere in each Universe – whether its result is recorded or not. Even the main proponent of this interpretation, B. de Witt, has confessed: “The idea is not easy to reconcile with common sense”. I agree.

(iv) *The quantum logic*. In desperation, some physicists turned philosophers have decided to dismiss the very logic we are using – in science and elsewhere, so that a statement like “the Bell inequalities are violated” would not make any definite sense. OK, if we dismiss the formal logic, I do not know how we can use any scientific theory and make any predictions - until the quantum logic experts tell us what to replace the classical logic with. To the best of my knowledge, so far they have not done that, at least for the measurement process. I personally trust J. Bell’s opinion: “It is my impression that the whole vast subject of Quantum Logic has arisen [...] from the misuse of a word.”

The weakness of all interpretations of quantum mechanics is that, as far as I know, neither of them has yet provided any suggestion how this particular interpretation might be tested experimentally to exclude other ones. On the positive side, there is a consensus that quantum mechanics makes correct, if sometimes probabilistic, predictions of all reliable experimental results we are aware of. Maybe, this is not that bad for a scientific theory.¹²

¹⁰ A detailed discussion of statistical ensemble’s role may be found, e.g., in L. Balentine, *Quantum Mechanics*, World Scientific, 1998.

¹¹ D. Bohm, *Phys. Rev.* **85**, 165; 180 (1952).

¹² If the reader is not satisfied with this “positivistic” approach, and wants to improve the situation, my earnest advice would be to start not from square one, but from reading what other (including some very clever!) people thought about it. A good starting point is the review collection by J. Wheeler and W. Zurek (eds.), *Quantum Theory and Measurement*, Princeton U. Press, 1983.